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Protonation Equilibria in Aqueous Solutions of Thiocarbohydrazide and Thiosemicarbazide

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The equilibria in aqueous solutions of thiocarbohydrazide have been determined potentiometrically at 25.0±0.1°C and compared with those found in solutions of thiosemicarbazide. In acidic media a two-step protonation equilibrium has been found for thiocarbohydrazide and a one-step protonation equilibrium for thiosemicarbazide; this corresponds to the number of hydrazinic radicals of the two molecules, thus suggesting that the protons are attached to the $-NH-NH_2$ group also in thiosemicarbazide. The dependence of the cumulative protonation constants β_n upon the ionic strength up to $\mu=2$ M is that typical for cation acids for both compounds. In alkaline media both compounds present a two-step protonation equilibrium. The dependence on the ionic strength of the protonation constants β_n^* in alkaline media is that typical for anion bases. These anions derive from thio-enolic forms of the molecules. The existence of cation acids and anion bases in the solutions has been checked also by electrophoretic tests. The stepwise constants for both compounds show a regular decrease as expected for polyprotic acids.

Introduction

The protonation equilibria in aqueous solutions of thiocarbohydrazide, $S=C(NH-NH_2)_2$ (abbrev. $H_m$tcaz) have been determined as a contribution to studies[1,2] on this compound, which is an efficient ligand in complexes. For comparison, also the protonation equilibria for thiosemicarbazide, $S=C(NH_2)-NH-NH_2$ (abbrev. $H_m$tscaz) have been determined.

Experimental Section

Reactants. Thiocarbohydrazide, CH_6N_4S, was prepared from aqueous solution of hydrazinium hydrazinedithiocarboxylate treated by acetic acid and sodium acetate (pH=8.5-9.0), m.p. 171°C. Thiosemicarbazide, CH_5N_3S was prepared by recrystallisation from alcohol of trade reagent.

Solutions. Standard solutions of $H_m$tcaz and $H_m$tscaz were prepared by dissolving weighed amounts of the product in known volumes of solutions.

Stock solution of hydrogen chloride was prepared and its concentration (molarity) determined both by weighing precipitated AgCl and by titrimetry with $KHCO_3$.

Solutions of potassium hydroxide were prepared following the prescriptions of Vogel[3] and their concentration determined by titrimetry. The volumes of the titrant solutions were measured with precision ±0.01 ml (0.1%).

Potassium chloride of reagent grade purity was recrystallized once before its use. Weighed amounts were added to the solutions in order to obtain the desired ionic strength.

Potentiometric Determinations. Potentiometric determinations were performed by a potentiometer Metrohm E 388, with a glass electrode Metrohm EA 107 UX. The glass electrode was calibrated with respect to $[H^+]$ with the same hydrochloric acid solutions used as tritrant. No special calibration of the instrument was made in alkaline media. Calomel electrode (KCl sat.) was used as reference. The reaction vessel, covered with a proper lid to avoid contamination from the air, was mantained at 25±0.1°C by circulation of thermostatized water. In every determination it was checked by return measurements that no decomposition had taken place; the data resulted reproducible within the experimental error.

Electrophoretic tests. The electrophoresis were conducted at 250 Volt and 20 mA on paper Whatman No. 1. The buffer solutions were prepared by adding to 0.1 *M* KCl solution convenient amounts of hydrochloric acid or potassium hydroxide. The spots were revealed by an iodine solution.

Results

Some representative titration curves are drawn in Figure 1. We shall describe separately the results obtained in acidic media and in alkaline media.

Acidic solutions. For thiocarbohydrazide the formation function[4]

$$\bar{n} = \frac{[a\text{–}H^+]}{C_A}$$

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[1] G. R. Burns, *Inorg. Chem.*, 7, 277 (1968).

[2] A. Braibanti, A. Tiripicchio, and M. Tiripicchio Camellini, in preparation.

[3] A. I. Vogel, «Quantitative Inorganic Analysis», Longmans.

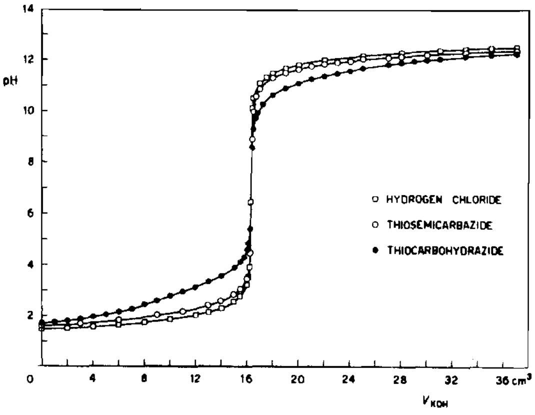

Figure 1. Typical titration curves of thiosemicarbazide ($H_m$tscaz) and thiocarbohydrazide ($H_m$tcaz) compared with hydrogen chloride.

where C_A is the total concentration of $H_m$tcaz and a is the concentration of the acid added, is represented in Figure 2. The data obtained fit well with a typical double protonation equilibrium. Analogous formation functions are obtained with solutions at higher ionic strength (KCl 0.1, 0.5, 1.0, 1.5, 2.0 M). The equilibria can be written as

$$H_mL+H^+ \rightleftarrows H_{m+1}L^+$$

$$H_{m+1}L^+ + H^+ \rightleftarrows H_{m+2}L^{2+}$$

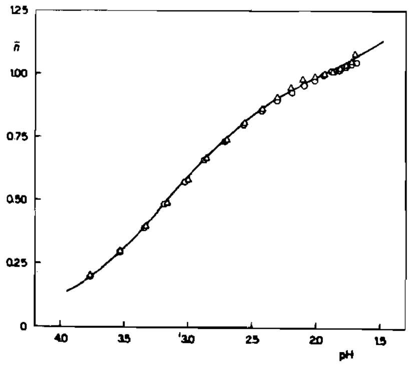

Figure 2. Protonation function $\bar{n}$ of $H_m$tcaz in acidic media. Continuous line calculated from $R_{av}=16.22$. ○ $C_A=2.1901\times10^{-2}\,M$; △ $C_A = 2.1592 \times 10^{-2}\,M$.

Table I. Calculation of R, log β_1, log β_2 for $H_m$tcaz in aqueous solution. $C_A=2.1901\times10^{-2}\,M$, $t=25°C$

$\bar{n}$	$-\log[H^+]$	$-\log \mathbf{a}$	R
1.0	1.925	0	—
0.8	3.772	0.645	15.75
0.7	2.786	0.861	16.25
0.6	2.980	1.055	16.50
0.5	3.156	1.231	17.00
0.4	3.329	1.404	16.75
0.3	3.524	1.595	17.15

$R_{av} = 16.57\,(47)$; $\log R = 1.219\,(12)$; $\log\beta_1 = 1.219\,(12)+1.913\,(12) = 3.132\,(24)$; $\log\beta_2=3.825\,(24)$.

The protonation cumulative constants, which can be written for a complex $H_{m+n}L^{n+}$

$$\beta_n = \frac{[H_{m+n}L^{n+}]}{[H_mL][H^+]^n}$$

were calculated following the graphical methods of Sillén.[5] The function

$$\bar{n} = \frac{R\,\mathbf{a}+2\,\mathbf{a}^2}{1+R\,\mathbf{a}+\mathbf{a}^2}$$

where $R=\beta_1\,.\,\beta_2^{-1/2}$ and $\mathbf{a}=a\,.\,\beta_2^{1/2}$ (being $a=[H^+]$), was plotted against log a. The value ½ log $\beta_2=-\log[H^+]_0$ with estimated standard deviation (e.s.d.) was calculated by averaging values of $-\log[H^+]$ at points symmetrical with respect to $\bar{n}=1$. In order to obtain mean R values with e.s.d. from several experimental points, a set of graphs at constant $\bar{n}$ ($\bar{n}=0.3$, 0.4, 0.5, 0.6, 0.7, 0.8) was prepared putting as variables R and $\log\mathbf{a}=\log[H^+]-\log[H^+]_0$. A typical calculation is quoted in Table I. The standard deviations quoted here refer to a single determination. An estimate of the accuracy can be obtained by averaging the values calculated from the two determinations reported in Figure 2. One obtains log $\beta_2=3.866\,(42)$. The calculation has been cheked by the Speakman[6] method (Figure 3). Several determinations were performed at different ionic strengths and the results are quoted in Table II. The logaritms of the constants

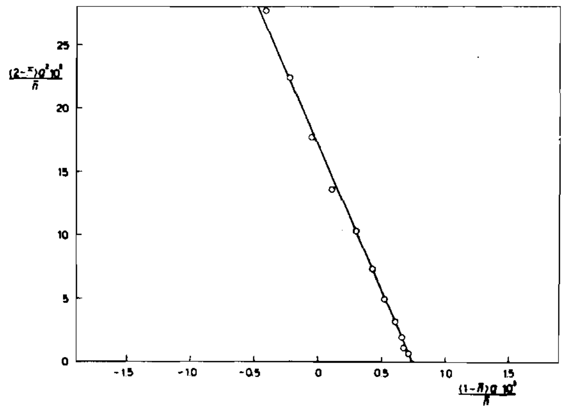

Figure 3. Calculation of cumulative constants of $H_m$tcaz according to Speakman. $a=[H^+]$; $C_A=2.1901\times10^{-2}\,M$.

Table II. Cumulative and stepwise protonation constants for $H_m$tcaz in acidic media.

C_A (M) $\times 10^2$	μ (M) KCl	logβ$_2$(σ)	logβ$_1$(σ)	logK$_2$(σ)
2.1901	0.01	3.825 (24)	3.132 (24)	0.693 (48)
2.1765	0.10	3.904 (21)	3.129 (28)	0.775 (49)
2.0380	0.50	3.968 (18)	3.159 (30)	0.809 (48)
2.2082	1.00	4.022 (10)	3.209 (18)	0.813 (28)
2.2082	1.50	4.282 (12)	3.330 (15)	0.952 (27)
2.2084	2.00	4.380 (12)	3.394 (10)	0.986 (22)

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(4) J. Bjerrum, «Metal Ammine Formation in Aqueous Solutions», P. Haase and S. Copenhagen (1941).
(5) L. G. Sillén, *Acta Chem. Scand.*, *10*, 186 (1956).
(6) J. C. Speakman, *J. Chem. Soc.*, *p.* 855 (1940).

when plotted against $\sqrt{\mu}$ (Figure 4) show a dependence which is typical for cation acids.[7] This result is confirmed by electrophoretic test: in solution at pH ~2.0 the spot migrates toward the cathode. Only one spot is observed. The calculations relative to thiosemicarbazide in acidic solutions show how only one protonation equilibrium must be taken into account. The equilibrium constants measured at different ionic strengths are quoted in Table III and the representative curves are drawn in Figure 5. Also for thiosemicarbazide in acidic media the dependence on the ionic strength (Figure 6) is that typical for cation acids.

Table III. Protonation constant for $H_m$tscaz in acidic media. $C_A = 2.6706 \times 10^{-2}$ M

μ (M) KCl	log β_1 (σ)
0.01	1.729 (18)
0.10	1.743 (15)
0.50	1.768 (12)
1.00	1.700 (15)
1.50	1.938 (10)
2.00	2.009 (12)

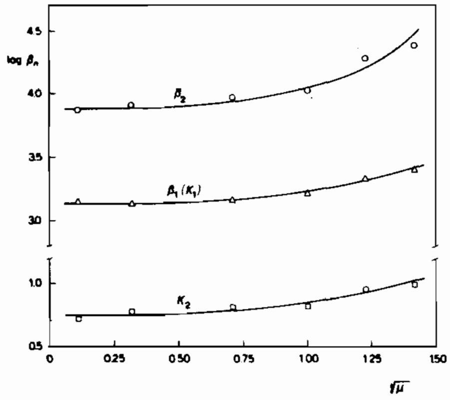

Figure 4. Dependence of cumulative and stepwise constants of $H_m$tcaz on ionic strength in acidic media.

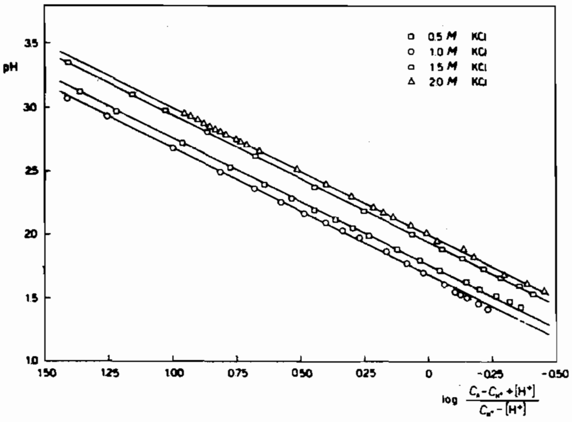

Figure 5. Determination of the protonation constant of $H_m$tscaz in acidic media. Continuous lines calculated from values of Table III. C_A=total concentration of $H_m$tscaz; C_{H^+}=added acid.

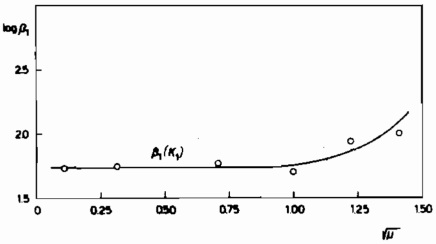

Figure 6. Dependence on ionic strength of the protonation constant of $H_m$tscaz in acidic media.

Alkaline solutions. In alkaline solution the data can be interpreted for both compounds $H_m$tcaz and $H_m$tscaz on the basis of a double protonation process

$$H_{m-2}L^{2-} + H^+ \rightleftarrows H_{m-1}L^-$$

$$H_{m-1}L^- + H^+ \rightleftarrows H_mL$$

or in general

$$H_{m-N'}L^{N'-} + n^* H^+ \rightleftarrows H_{m-n'}L^{n'-}$$

where $n' = N' - n^*$ and n^* indicates the protonation steps in alkaline media with cumulative formation constants

$$\beta_n^* = \frac{[H_{m-n'}L^{n'-}]}{[M_{m-N'}L^{N'-}][H^+]^{n^*}}$$

This symbolism has been adopted because the determination of the most deprotonated form $H_{m-N'}L^{N'-}$ is questionable and whenever an even more deprotonated form would be discovered, all the subsequent protonation constants in alkaline and acidic fields should be changed. Therefore the cumulative constants will be numbered β_1, β_2, ... β_n in acidic media and β_1^*, β_2^*, ... β_n^* in basic media. In basic media the deprotonation function is considered

$$\bar{n} = \frac{[b - OH^-]}{C_A}$$

where b is the concentration of added KOH from the equivalence point and OH^- is measured potentiometrically; C_A is the total concentration of H_mL ($H_m$tcaz or $H_m$tscaz, respectively). If the maximum deprotonation step is 2 ($N' = 2$), then the protonation function $\bar{n} = 2 - \bar{n}'$ can be calculated. With the same procedure as for the equilibria in acidic solutions, $-\log[H^+]_0 = \frac{1}{2}\log \beta_2^*$, and values of R were obtained; from these, log β_1^* was calculated. The measurements were repeated at different ionic strengths.

Although the determinations of the protonation constants in alkaline solutions are unprecise due to the incorrect response of the glass electrode and to other causes, nonetheless the data obtained exclude the existence of a one-step deprotonation process both in solutions of $H_m$tcaz and $H_m$tscaz. The data of log β_n^* plotted against the square root of the ionic strength show for both compounds a behavior typical for anion bases.[7] The deprotonation function $\bar{n}'$ for

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(7) E. J. King, «Acid-base Equilibria», Pergamon Press, Oxford, p. 274 (1965).

Table IV. Cumulative and stepwise protonation constants for $H_m$tcaz in alkaline media. $C_A = 2.1893 \times 10^{-2}$ M

μ (*M*) KCl	log β_2^* (σ)	log β_1^* (σ)	log K_2^* (σ)
0.01	23.77 (6)	12.36 (11)	11.41 (17)
0.10	23.75 (6)	12.44 (9)	11.31 (15)
0.50	23.65 (4)	12.34 (12)	11.31 (16)
1.00	23.72 (6)	12.37 (14)	11.35 (20)
1.50	23.75 (8)	12.40 (14)	11.35 (22)
2.00	23.71 (7)	12.37 (14)	11.34 (21)

Table V. Cumulative and stepwise protonation constants for $H_m$tscaz in alkaline media. $C_A = 2.6675 \times 10^{-2}$ M

μ (*M*) KCl	log β_2^* (σ)	log β_1^* (σ)	log K_2^* (σ)
0.01	24.82 (8)	12.66 (28)	12.16 (36)
0.10	24.61 (4)	12.67 (17)	11.94 (21)
0.50	24.58 (3)	12.54 (15)	12.04 (18)
1.00	24.51 (5)	12.46 (19)	12.05 (24)
2.00	24.69 (3)	12.57 (12)	12.12 (15)

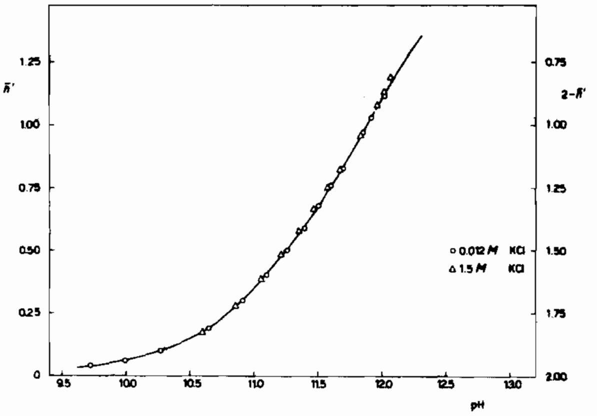

Figure 7. Deprotonation function $\bar{n}'$ (or protonation function 2-$\bar{n}'$) for $H_m$tcaz in alkaline media. Continuous line calculated with $R_{av} = 3.16$. C_A = total concentration of $H_m$tcaz = 2.1893 × 10^{-2} *M*.

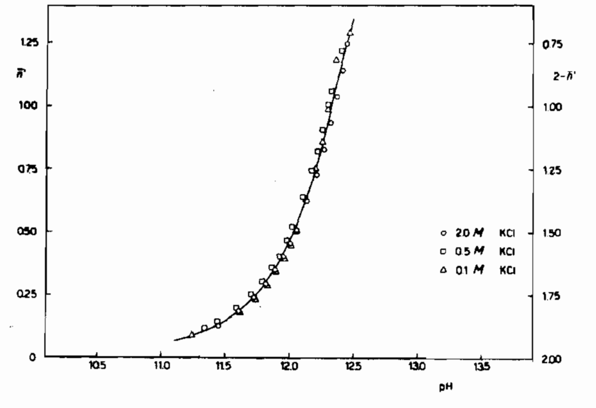

Figure 8. Deprotonation function $\bar{n}'$ (or protonation function 2-$\bar{n}'$) for $H_m$tscaz in alkaline media. Continuous line calculated with $R_{av} = 0.53$. C_A = total concentration of $H_m$tscaz = 2.6675 × 10^{-2} *M*.

solutions of $H_m$tscaz is represented in Figure 7; the same function for solutions of $H_m$tscaz is represented in Figure 8. The determinations, repeated at different ionic strengths, are quoted for $H_m$tcaz in Table IV and for $H_m$tscaz in Table V. The dependence of log β_n^* on the ionic strength (Figure 9) shows the same trend as for the acetato anion.[7] This result is confirmed by the electrophoretic test: in solutions at pH ~ 12 the spot migrates toward the anode. Only one spot is observed.

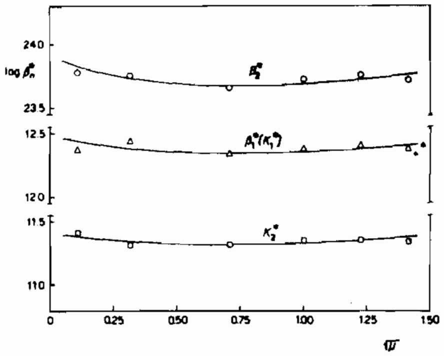

Figure 9. Dependence on the ionic strength of the protonation constants of $H_m$tcaz in alkaline media.

Discussion

The existence of cationic forms is proved either by the electrophoretic tests and by the dependence of the formation constants on the ionic strength, which resembles very closely that for glycinium ion.[7] The two-step protonation process for $H_m$tcaz and the one-step protonation process for $H_m$tscaz indicate that the protons are probably attached not only in $H_m$tcaz but also in $H_m$tscaz to the hydrazinic radicals which are two in $H_m$tcaz and one in $H_m$tscaz, thus forming cations with positive groups $-NH-NH_3^+$. A further support to this interpretation is given by the fact that the amino groups $-NH_2$ in urea and thiourea posses very weak basic properties. The acids H_{m+1}tcaz$^+$ is weaker than H_{m+1}tscaz$^+$; both are much stronger than $^+H_3N-NH_2$ (log $K_1 = 7.99$ [8]) very likely because they are thioamides. The molar fractions α_c of each component in acidic solutions of $H_m$tcaz are represented in Figure 10.

In weakly acidic and neutral solutions, the neutral molecules $H_m$tcaz and $H_m$tscaz must be largely preferred, because they constitute the crystals.[2,9] In the crystals the molecule of $H_m$tcaz[2] presents one hydrazinic radical $-NH-NH_2$ turned toward the $S=C<$ group (*cis* configuration) while in the molecule of $H_m$tscaz[9] the unique $-NH-NH_2$ group is turned opposite to $S=C<$ (*trans* configuration). Anyway the energy barrier to be overhelmed for the rotation around the bond C–N must be not too high, because $H_m$tscaz very easily forms complexes with *cis* structure; therefore both *cis* and *trans* configurations

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(8) G. C. Ware, J. B. Spulnik, and E. C. Gilbert, *J. Am. Chem. Soc.*, *58*, 1605 (1936).

(9) P. Domiano, G. Fava, and M. Nardelli, *Ric. Sci.*, 36, 744 (1966).

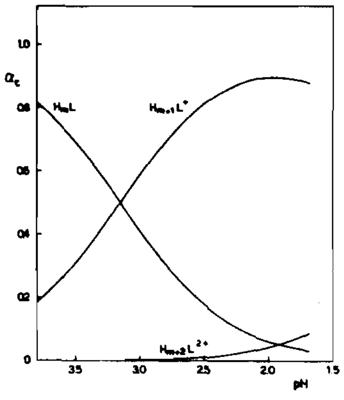


Figure 10. Fractions α_c of ionic species in acidic solutions of $H_m$tcaz.

Table VI. Stepwise protonation constants for $H_m$tcaz and $H_m$tscaz in aqueous solution

Protonated species	$H_m$tcaz	$H_m$tscaz
$H_{m+2}L^{2+}$	$\log K_2 = 0.693$	
$H_{m+1}L^+$	$\log K_1 = 3.132$	$\log K_1 = 1.728$
H_mL	$\log K_2^* = 11.41$	$\log K_2^* = 12.16$
$H_{m-1}L^-$	$\log K_1^* = 12.36$	$\log K_1^* = 12.66$

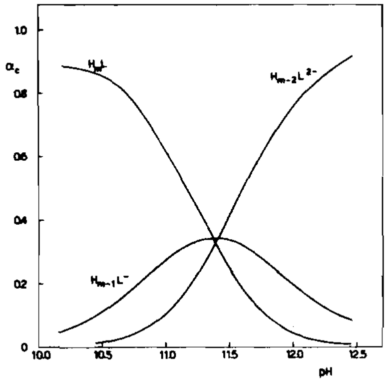
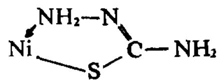


Figure 11. Fractions α_c of ionic species in alkaline solutions of $H_m$tcaz.

are assumed as possible in solution. The successive deprotonation steps can be explained by mean of thioenolic forms of the molecules, by transfer of one proton from –NH– to S. These forms could also give origin to ampholytic species. The electrophoretic tests and the dependence of the protonation constants on the ionic strength in alkaline media confirm the existence of anion bases in such solutions. For H_m tscaz a complex with the ring



has been found in the solid state in the salt Ni(H_{m-1}tscaz)₂.[10] More uncertain is the constitution of the least protonated forms because no sure argument demonstrates which of the hydrogen atoms has been detached as proton in the dissociation reaction. The molar fractions α_c of each component in alkaline solutions of $H_m$tcaz are represented in Figure 11.

On the whole, the step-wise constants (Table VI) show a very regular decrease, as expected for polyprotic acids.

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(10) L. Cavalca, M. Nardelli, and G. Fava, *Acta Cryst.*, *15*, 1139 (1962).