

Note

PROTONATION THERMODYNAMICS OF THIOVIOLURIC ACID

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This paper presents pH-metric and spectrophotometric studies of the protonation of thiovioluric acid in aqueous medium. One motivation for this study comes from uses of this acid [1–4] as a suitable reagent for spectrophotometric determination of several metals. The protonation constants are pre-requisites in studying its association with other ions. Up to this point, information regarding the protonation of thiovioluric acid is incomplete. Lal and Dutt [5] reported only pK_1 , but pK_2 and pK_3 values of this acid have not been reported.

EXPERIMENTAL

The thiovioluric acid (TVA) was synthesized using the method of Lal and Dutt [5] and was used after further purification. All other chemicals of AnalaR grade were used without further treatment. The setup for the potentiometric titrations of thiovioluric acid was

Ag, AgCl(HCl) glass(KCl, TVA, HClO₄–NaClO₄, NaOH) KCl, Hg₂Cl₂, Hg
(to maintain $I = 0.1$ M)

The pH values measured with an expanded scale pH-meter (ELICO Model No. pH 821, Hyderabad, India) were corrected from the calibration curves to obtain the true pH values.

In the spectrophotometric studies the method of Stenstorm and Goldsmith [6] was followed. The absorbance of each solution at a particular pH and at a constant ionic strength was measured between 220 and 600 nm in a 1 cm cell with a Specord recording spectrophotometer (Carl-Zeiss) and Spectronic-20 (Bausch and Lomb) correct to ± 0.01 absorbance unit. The sodium hydroxide solutions of known pH were prepared using published methods just prior to the measurements, flushed with nitrogen to exclude carbon dioxide, and the high pH experimental solutions were kept in vessels with KOH guard tubes during use. The pK values have been calculated with an accuracy of 0.01 from the inflexion point of the pH profile of the

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absorbance measured at several suitable wavelengths in the UV and visible regions at pH intervals of 0.10–0.20.

RESULTS AND DISCUSSION

The pH of the medium has a marked effect on the spectra of thiovioluric acid in solution. At moderate acidity (pH = 4.0), the three bands at 222, 260 and 340 nm were observed. At low pH, the bands at 222 nm and 340 nm disappear and the 260 nm band becomes prominent. In the presence of base, the band at 260 nm disappears and the bands at 222 nm and 340 nm gradually become prominent. A new band in the visible region between 580 and 583 nm also appears. At pH beyond 10.0, the band at 340 nm is shifted to 350 nm with an isobestic point at 347 nm. At very high pH greater than 13.60, the band at 350 nm is shifted to 325 nm and the band at 222 nm disappears. This spectral behaviour of thiovioluric acid solution at different pH can be interpreted in terms of the formation of different protonation–deprotonation equilibria.

Thiovioluric acid ($C_4H_3O_3N_3S$) shows stepwise protonation as characterized by the constants

$$K_1 = \frac{[HA^{2-}]}{[H^+][A^{3-}]}, \quad K_2 = \frac{[H_2A^-]}{[H^+][HA^{2-}]}, \quad K_3 = \frac{[H_3A]}{[H_2A^-][H^+]}$$

From the potentiometric titrations of $HClO_4$ in the absence and presence of TVA, formation curves in which \bar{n}_A (the average number of protons bound per free ligand) was plotted against pH were constructed in accordance with the procedure of Irving and Rossotti [7]. By applying Bjerrum's [8] half integral method, the stepwise protonation constants at three temperatures were determined, the corrections for the activity coefficient were applied on the basis of Davies' equation [9] and the thermodynamic functions were also evaluated. Table 1 compiles the final values of all the measurements.

In Fig. 1, the absorbance has been shown as a function of pH. The existence of isobestic points in different pH regions suggests the occurrence of different species in the solutions related by pH-dependent equilibria. The inflexion points in the three pH domains, as shown in Fig. 1, and also calculated for several other wavelengths, give the values of the protonation constants. These have also been converted to thermodynamic K^1 values and ΔG , ΔH , and ΔS values have also been calculated and are given in Table 1. The $\log K_1$, $\log K_2$ and $\log K_3$ values decreased linearly with $1/T$ in each case, indicating a constant ΔH for the stepwise protonations.

The variation of the UV–visible absorption spectrum with pH can be correlated with the proton dissociations of the 2,4-hydroxyl group substituents and the 5-oxime group. The resonance structures indicate that the oxime proton will be the first to dissociate. The spectral studies under different pH conditions by Resnik and Wolff [10] on the homologous violuric acid which exhibits identical spectral behaviour, the only difference being that all the UV bands observed in violuric acid [11] show red shifts by 8–25

TABLE 1

Thermodynamic protonation constants and other thermodynamic parameters

Temp. (°C)	First protonation			Second protonation			Third protonation					
	$\log K_1^1$	$-\Delta G$ (kJ mole ⁻¹)	$-\Delta H$ (kJ mole ⁻¹)	ΔS (J deg ⁻¹ mole ⁻¹)	$\log K_2^1$	$-\Delta G$ (kJ mole ⁻¹)	$-\Delta H$ (kJ mole ⁻¹)	ΔS (J deg ⁻¹ mole ⁻¹)	$\log K_3^1$	$-\Delta G$ (kJ mole ⁻¹)	$-\Delta H$ (kJ mole ⁻¹)	ΔS (J deg ⁻¹ mole ⁻¹)
18	14.42 ±0.02	19.13 ±0.05	5.46 ±0.25	84.50 ±0.85	10.88 ±0.02 11.15 ^a ±0.02	14.43 ±0.07 14.79 ^a ±0.03	4.28 ±0.28 5.35 ^a ±0.24	64.29 ±0.08 69.20 ^a ±0.70	4.68 ±0.06 4.59 ^a ±0.05	6.21 ±0.08 6.09 ^a ±0.08	3.89 ±0.22 3.79 ^a ±0.28	34.70 ±0.78 33.95 ^a ±0.72
31	14.25 ±0.03	19.75 ±0.08	5.46 ±0.25	82.92 ±0.95	10.74 ±0.02 10.95 ^a ±0.05	14.88 ±0.08 15.17 ^a ±0.06	4.28 ±0.28 5.35 ^a ±0.24	63.02 ±0.83 67.50 ^a ±0.89	4.55 ±0.05 4.48 ^a ±0.04	6.30 ±0.08 6.22 ^a ±0.03	3.89 ±0.22 3.79 ^a ±0.28	33.51 ±0.80 32.92 ^a ±0.58
42	14.12 ±0.05	20.28 ±0.02	5.46 ±0.25	81.72 ±0.92	10.62 ±0.03 10.84 ^a ±0.92	15.25 ±0.05 15.57 ^a ±0.04	4.28 ±0.28 5.35 ^a ±0.24	62.00 ±0.87 66.64 ^a ±0.85	4.46 ±0.08 4.37 ^a ±0.06	6.40 ±0.05 6.27 ^a ±0.08	3.89 ±0.22 3.79 ^a ±0.28	32.66 ±0.95 31.93 ^a ±0.89

^a Potentiometrically determined values.

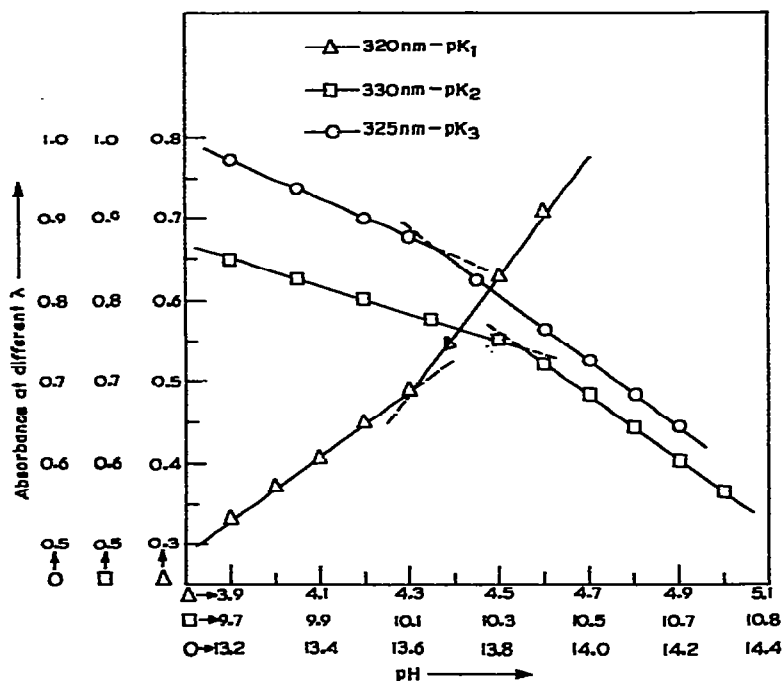


Fig. 1. Absorbance as a function of pH. The concentration of thiovioluric acid was 5.0×10^{-5} M in each case.

nm in TVA, corroborate this view. It is clear from the data that the general tendency of the UV and visible bands is to shift towards longer wavelengths and stronger absorptions with increasing pH, parallel to the enhanced deprotonation. Since deprotonation increases the electron donation of the hydroxyl and oxime groups, this agrees with the fact that stronger electron donation or withdrawal in the benzenoid system leads to a shift to longer wavelengths [12]. The spectra of thiovioluric acid in phosphate and borate buffers of pH 6.20 and 6.0, respectively, tally with the spectra of the aqueous solutions of the same pH. In the high pH domain (9.5) two different buffers, viz. borate + NaOH and glycine + NaOH, have been used. Relative to the carbonate, phosphate or alkaline system, the borate and the glycine system show a red shift and weaker absorbance at the band peak. Possibly the specific interaction of the B—O—H or N—H group with the oxime nitrogen reduces its interaction with the π electrons of the ring system. This is similar to the effect of *para* substituents in the benzenoid system as explained earlier [12].

This result seems to imply that a structural change other than that of deprotonation may occur at high pH. As a test, solutions of thiovioluric acid in borate (pH = 9.20) and phosphate (6.0) buffers were subjected to sudden pH stress and investigated spectrophotometrically. There is exact agreement between the two sets of spectra before and after the treatment, and with the spectra of the solution not subjected to the sudden pH stress. Since the spectral profile is not changed and the changes in absorbance can be accounted for by the changes in concentration, this indicates that same

protonation equilibria are present in the buffered media also, the controlling factor being solely the pH of the medium. Generally, the enthalpy changes in any chemical reaction are associated with breaking and formation of bonds. In the protonation of thiovioluric acid, the sources of enthalpy change are the bond formation between the proton and the anion and the resulting changes in water structure. Treating this as a ligand exchange reaction of the protons and considering that thioviolurate ions are soft acceptors compared to water, the reactions must be exothermic. In the consecutive protonation processes there is no significant change in the type of bonding; so the enthalpy values are likely to be of the same magnitude, as is evident from Table 1. The entropy changes associated with progressive protonation are: (1) charge neutralization; (2) subsequent liberation of ordered water molecules; and (3) loss of rotational and vibrational degrees of freedom of the ligand. Only (3) gives a small negative contribution to entropy, but the contributions of (1) and (2) together more than offset that due to (3), and hence all steps have large positive ΔS values. The protonation of thiovioluric acid then appears to be entropy driven, as expected from the degree of charge neutralization and polarizability of the resulting anions.

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