Thermochimica Acta, 64 (1983) 139–148
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMODYNAMIC PROTON–LIGAND STABILITY CONSTANTS IN DIOXANE–WATER MEDIA. pk_a, ΔG^0, ΔH^0 AND ΔS^0 VALUES FOR 1,3-DISUBSTITUTED THIOVIOLURIC ACIDS

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(Received 25 October 1982)

ABSTRACT

Thermodynamic protonation constants (pK_a^T) of diphenylthiovioluric acid (DPTVA), di-*p*-tolylthiovioluric acid (D-*p*-TTVA), di-*m*-tolylthiovioluric acid (D-*m*-TTVA), di-*o*-tolylthiovioluric acid (D-*o*-TTVA), di-*o*-xylylthiovioluric acid (D-*o*-XTVA), di-*m*-xylylthiovioluric acid (D-*m*-XTVA)di-*p*-xylylthioviolyric acid (D-*p*-XTVA), di-*p*-anisylthiovioluric acid (D-*p*-ATVA) and di-*o*-anisylthiovioluric acid (D-*o*-ATVA) have been determined potentiometrically in different mole fractions of dioxane (0.174–0.350) at 20, 30 and 35 ± 0.1°C. The pK_a^T values do not vary linearly with the reciprocal of the dielectric constant of the medium, but a plot of pK_a^T vs. the mole fraction of dioxane is linear at all the given temperatures. The effects of temperature, solvent and the change from mixed aqueous to aqueous media are briefly discussed.

INTRODUCTION

Thiovioluric acids have found immense analytical applications [1–5]. However, such applications necessitate a precise knowledge of their protonation constants. Recently, several analogous compounds have been synthesised by the introduction of substituent groups in different positions for improved analytical characteristics. This empirical approach, although sometimes inescapable, is generally wasteful and it is more fruitful to determine the physico-chemical properties of the reagents and their resulting metal complexes, and in particular their protonation constants, which could lead to a better understanding of the cause of specificity and selectivity of relevant analytical reactions. With this in view, the thermodynamic protonation

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0040-6031/83/$03.00

constants, pK_a^T, of substituted thiovioluric acids in different mole fractions of dioxane at 20, 30 and 35 ± 0.01°C have been determined and the thermodynamic functions associated with the protonation process evaluated.

EXPERIMENTAL

All the thiovioluric acids were synthesised using the method described elsewhere [6], recrystallised before use, and the purity was checked by elemental analysis, UV and IR spectra. All other chemicals used were of AnalaR and G.R. grades of B.D.H. or E. Merck unless otherwise stated. Dioxane was purified using the method of Weissberger et al. [7]. Carbonate-free sodium hydroxide was prepared by the electrolytic method of Vogel [8].

The protonation constants were determined by the pH-titration method employing a pH-meter cell of the type

Ag, AgCl|HCl|glass|KCl, Acids, $HClO_4$–$NaClO_4$, NaOH|KCl|Hg_2Cl_2

(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. From the potentiometric titrations of $HClO_4$ in the absence and presence of thiovioluric acids, formation curves in which $\bar{n}_A$ (the average number of protons bound per free ligand) plotted against pH were constructed in accordance with the procedure of Irving and Rossotti [9]. By applying Bjerrum's [10] half integral method, the protonation constants at three temperatures were determined, the corrections for the activity coefficient were applied on the basis of Davies' equation [11] and the thermodynamic protonation constants were evaluated. The change in free energy, ΔG^0, enthalpy, ΔH^0, and entropy, ΔS^0, associated with the protonation equilibrium, i.e.

$$H^+ + A^- \rightleftharpoons HA$$

can be readily evaluated on the basis of eqns. (1)–(3)

$$-\Delta G^0 = 2.303RT \log K_T \tag{1}$$

$$\frac{d \log K_T}{d(1/T)} = \frac{-\Delta H^0}{4.57} \tag{2}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{3}$$

RESULTS AND DISCUSSION

The protonation constants at 20, 30 and 40°C are given in Table 1. The average pK_a^T generally falls within a spread of ±0.02 but not beyond ±0.03

TABLE 1

pK_a^T values of N,N'-disubstituted thiovioluric acids at different temperatures

Acid	Mole fraction of dioxane (n_2)											
	0[a]			0.174			0.250			0.350		
	20°C	30°C	40°C	20°C	30°C	40°C	20°C	30°C	40°C	20°C	30°C	40°C
DPTVA	4.67	4.56	4.45	5.49	5.36	5.24	5.88	5.76	5.64	6.45	6.31	6.18
D-*p*-TTVA	4.90	4.82	4.72	5.82	5.69	5.58	6.24	6.09	5.98	6.75	6.60	6.48
D-*m*-TTVA	4.55	4.47	4.38	5.36	5.27	5.18	5.73	5.61	5.52	6.23	6.12	6.02
D-*o*-TTVA	4.40	4.29	4.20	5.05	4.96	4.88	5.48	5.37	5.28	5.93	5.81	5.70
D-*o*-XTVA	4.45	4.33	4.23	5.12	5.03	4.94	5.52	5.41	5.32	6.00	5.88	5.78
D-*m*-XTVA	4.85	4.76	4.65	5.72	5.60	5.50	6.08	5.96	5.85	6.63	6.50	6.38
D-*p*-XTVA	4.51	4.40	4.30	5.34	5.24	5.15	5.68	5.57	5.48	6.18	6.07	5.98
D-*p*-ATVA	4.77	4.68	4.60	5.62	5.52	5.41	5.97	5.88	5.80	6.54	6.43	6.34
D-*o*-ATVA	4.48	4.37	4.28	5.19	5.10	5.02	5.57	5.46	5.37	6.05	5.93	5.82

[a] Extrapolated values at 0% dioxane.

TABLE 2

Empirical correlation of pK_a^T with mole fraction of dioxane (n_2)

Acid	Temp. (°C)	$pK_a^T = mn_2 + C$					Acid	Temp. (°C)	$pK_a^T = mn_2 + C$				
		Least-squares method			Graphically				Least-squares method			Graphically	
		m	*C*	*r*	*m*	*C*			*m*	*C*	*r*	*m*	*C*
DPTVA	20	6.08	4.36	1.00	6.05	4.38	D-*m*-XTVA	20	6.02	4.78	0.99	5.08	4.80
	30	6.06	4.30	1.00	6.03	4.30		30	6.00	4.72	1.00	5.06	4.73
	40	6.06	4.21	0.99	6.04	4.22		40	6.02	4.66	1.00	5.05	4.67
D-*p*-TTVA	20	5.60	4.94	0.99	5.58	4.95	D-*p*-XTVA	20	5.22	4.39	1.00	5.18	4.40
	30	5.58	4.87	1.00	5.55	4.87		30	5.20	4.33	1.00	5.16	4.34
	40	5.57	4.77	0.99	5.54	4.78		40	5.20	4.27	1.00	5.14	4.27
D-*m*-TTVA	20	5.05	4.50	1.00	5.02	4.50	D-*p*-ATVA	20	5.58	4.60	0.99	5.55	4.62
	30	5.04	4.45	1.00	5.02	4.45		30	5.58	4.54	1.00	5.55	4.55
	40	5.02	4.38	0.99	5.00	4.39		40	5.55	4.45	1.00	5.52	4.46
D-*o*-TTVA	20	5.02	4.19	1.00	4.98	4.20	D-*o*-ATVA	20	4.63	4.34	1.00	4.58	4.35
	30	5.03	4.14	1.00	4.98	4.14		30	4.62	4.30	1.00	4.57	4.30
	40	5.00	4.17	1.00	4.96	4.08		40	4.60	4.21	1.00	4.58	4.24
D-*o*-XTVA	20	5.76	4.35	1.00	5.72	4.35							
	30	5.76	4.27	1.00	5.72	4.28							
	40	5.75	4.22	1.00	5.70	4.23							

TABLE 3

ΔG^0, ΔH^0 and ΔS^0 values for thiovioluric acids at 30°C

Acid	Mole fraction of dioxane (n_2)											
	0 [a]			0.174			0.250			0.350		
	$-\Delta H^0$	$-\Delta G^0$	$+\Delta S^0$	$-\Delta H^0$	$-\Delta G^0$	$+\Delta S^0$	$-\Delta H^0$	$-\Delta G^0$	$+\Delta S^0$	$-\Delta H^0$	$-\Delta G^0$	$+\Delta S^0$
DPTVA	4.56	6.30	5.74	4.93	7.40	8.15	4.94	7.95	9.93	5.28	8.71	11.32
D-*p*-TTVA	5.19	6.65	4.82	5.56	7.86	7.59	5.58	8.41	9.34	5.92	9.11	10.52
D-*m*-TTVA	6.53	6.17	6.53	4.56	7.28	8.97	4.59	7.75	10.42	4.88	8.45	11.78
D-*o*-TTVA	8.11	5.92	8.11	3.83	6.85	9.90	3.85	7.42	11.78	4.12	8.02	12.87
D-*o*-XTVA	7.09	5.98	7.09	4.19	6.94	9.07	4.21	7.47	10.75	4.48	8.12	12.01
D-*m*-XTVA	7.55	6.57	7.55	5.05	7.73	8.84	5.08	8.23	10.39	5.38	8.98	11.88
D-*p*-XTVA	6.66	6.07	6.66	4.37	7.23	9.43	4.38	7.69	10.92	4.66	8.38	12.27
D-*p*-ATVA	7.02	6.46	7.02	4.97	7.62	8.74	5.01	8.12	10.26	5.32	8.88	11.74
D-*o*-ATVA	7.55	6.03	7.55	4.21	7.04	9.33	4.33	7.54	10.59	4.52	8.19	12.11

ΔG^0 and ΔH^0 in kcal mole^{-1}; ΔS^0 in cal mole^{-1} K^{-1}.

[a] Extrapolated values at 0% dioxane.

in any case. The empirical data for the mole fraction of dioxane (n_2) and ΔG^0, ΔH^0 and ΔS^0 values are given in Tables 2 and 3, respectively. The pK_a^T values increase with increase in dioxane content because of the decrease in the dielectric constant of bulk solvent. As the dielectric constant decreases, the ion interaction involving the proton and anionic oxygen on the ligand decrease to a greater extent than the ion dipole interaction between the proton and the solvent molecule. A plot of pK_a^T against mole fraction of dioxane (n_2) (Fig. 1) shows a linear relationship of the form $pK_a^T = mn_2 + C$.

As shown by Gurney [12] and others [13,14], the standard free energy change associated with the proton transfer, $\Delta G^0_{\text{diss.}}$, may be split into two distinct parts: electrostatic (el.) and nonelectrostatic (nonel.)

$$\Delta G^0_{\text{diss.}} = \Delta G^0_{\text{el.}} + \Delta G^0_{\text{nonel.}} \tag{4}$$

The electrostatic contribution to free energy change is often estimated using the Born equation [15]

$$\Delta G^0_{\text{el.}} = W = \frac{Ne^2}{2D}\left(\frac{1}{R_+} + \frac{1}{R_-}\right) \tag{5}$$

where R_+ and R_- are the radii of the solvated ions and D is the dielectric constant of the medium [16,17]. Hence

$$\Delta G^0_{\text{diss.}} = \Delta G^0_{\text{nonel.}} + \frac{Ne^2}{2D}\left(\frac{1}{R_+} + \frac{1}{R_-}\right) \tag{6}$$

Further, as $\Delta G^0_{\text{diss.}} = 2.303RT\,pK_a^T$ [16], the equation simplifies as

$$pK_a^T = \frac{\Delta G^0_{\text{nonel.}}}{2.303RT} + \frac{Ne^2}{4.606RTD}\left(\frac{1}{R_+} + \frac{1}{R_-}\right) \tag{7}$$

Conventionally, pK_a^T is plotted against $1/D$ assuming $\Delta G^0_{\text{nonel.}}$ to be indepen-

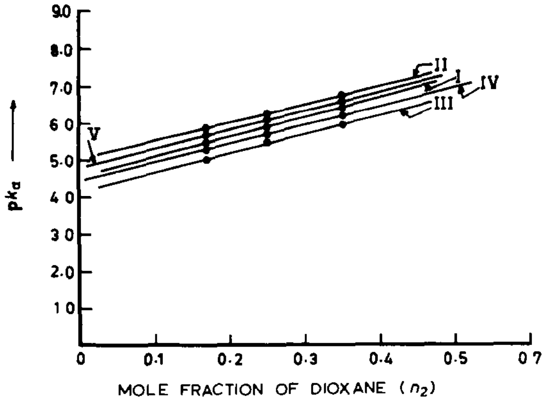

Fig. 1. Plot of pK_a^T against mole fraction of dioxane for I, DPTVA; II D-*p*-TTVA; III, D-*o*-TTVA; IV, D-*m*-TTVA; V, D-*m*-XTVA.

dent of the solvent. When the pK_a^T values of substituted thiovioluric acids are plotted against $1/D$ it is observed that the plots possess a distinct curvature. It seems evident that non-electrostatic factors exert a considerable influence on the diprotonation of thiovioluric acids.

For thiovioluric acids, the change in pK_a^T with mole fraction of dioxane (n_2) is of considerable magnitude. Generally, the difference in pK_a^T in aqueous medium ($n_2=0$) and aqueous dioxane medium ($n_2=0.350$) is of the order of 1.5–2.0 pK_a^T units. When pK_a^T values of these thiovioluric acids are plotted against n_2, straight-line relationships are encountered (Fig. 1). The experimental values of pK_a^T here indicate a maximum deviation from linearity of the order of 0.05 or about 0.5% in pK_a^T.

The goodness of fit in these instances was judged by calculating the correlation coefficient, r, defined by

$$r=\sum(x-\bar{x})(y-\bar{y})/\left[\sum(x-\bar{x})^2\sum(y-\bar{y})^2\right]^{1/2}$$

where $\bar{x}$ and $\bar{y}$ are the mean values of $x(pK_a^T)$ and $y(n_2)$, respectively. The summations are extended to all pairs (x, y) available. Linear proportionality is readily indicated between the variables when the value of r is $+1.0$ [18].

Since the value of r is approximately $+1.0$, at 20, 30 and 40°C for all the substituted thiovioluric acids [Table 2], it implies that there is quite a high probability of a linear relationship between pK_a^T and n_2. A similar behaviour is found for several other acids such as benzoic, acetic, propionic and formic acids [19] in aqueous dioxane. Likewise, linear proportionality is also obtained for some other mixed water solvents, e.g., acetic, propionic, butyric and benzoic acids in methanol–water mixtures [20].

The pK_a^T values have been determined with a precision of ± 0.02 to ± 0.03 and hence the error in ΔG^0 is believed to be close to ± 0.03 and ± 0.04 kcal mole^{-1}. The values of ΔS^0 given in Table 3 are accurate to ± 0.20 cal mole^{-1} K^{-1}.

The negative value of ΔH^0 found in aqueous as well as aqueous dioxane mixtures for all thiovioluric acids proves that their protonation at temperatures up to 40°C is exothermic. The negative value of ΔH^0 encountered here may be ascribed to the formation of the covalent bond between proton and anionic oxygen on the thiovioluric acids. Further, it is evident that the magnitude of change in ΔH^0 with solvent composition is relatively small and falls within the range of experimental error. It is because of this that the slopes of straight lines in the plots of pK_a^T against n_2 (Fig. 1) do not differ markedly and are nearly the same and parallel at the three temperatures for all the thiovioluric acids.

The values of ΔS^0 are found to increase with increase in dioxane content of the solvent medium for all the thiovioluric acids, thereby proving that it is dependent of solvent composition. The net entropy changes associated with the protonation process can be attributed to a combination of the following:

TABLE 4

$\Delta pK_a^T(S-W) = pK_a^T(S) - pK_a^T(W)$

Acid	Mole fraction of dioxane (n_2)								
	0.174			0.250			0.350		
	20°C	30°C	40°C	20°C	30°C	40°C	20°C	30°C	40°C
DPTVA	0.82	0.80	0.79	1.21	1.20	1.19	1.78	1.76	1.73
D-*p*-TTVA	0.92	0.87	0.86	1.34	1.27	1.26	1.85	1.78	1.76
D-*m*-TTVA	0.81	0.80	0.80	1.18	1.14	1.14	1.68	1.65	1.64
D-*o*-TTVA	0.65	0.67	0.68	1.08	1.08	1.08	1.53	1.52	1.50
D-*o*-XTVA	0.67	0.70	0.71	1.07	1.08	1.09	1.55	1.55	1.55
D-*m*-XTVA	0.87	0.84	0.85	1.23	1.20	1.20	1.78	1.74	1.73
D-*p*-XTVA	0.83	0.84	0.85	1.17	1.17	1.18	1.67	1.67	1.68
D-*p*-ATVA	0.85	0.84	0.81	1.20	1.20	1.77	1.77	1.75	1.74
D-*o*-ATVA	0.71	0.73	0.74	1.09	1.08	1.09	1.57	1.56	1.54

(i) charge neutralisation; (ii) subsequent liberation of ordered water molecules; and (iii) loss of rotational and vibrational degrees of freedom of the ligand. Only (iii) gives a small negative contribution to entropy, but the contributions of (i) and (ii) together more than offset that due to (iii) and hence the protonation process has large positive ΔS^0 values. The protonation of these acids then appears to be entropy driven as expected from the degree of charge neutralisation and polarizability of the resulting anions.

When the acid protonates in two media, the free energy change for the transfer reaction from one medium to the other is given by $2.303RT\,\Delta pK_a^T$. For instance with DPTVA, $\Delta G^0_{(\mathrm{aq.})}$ and $\Delta G^0_{(n_2=0.174)}$ are 6.30 and 7.40 kcal mole^{-1}, respectively, at 30°C, and ΔG^0 changes by 1.10 kcal mole^{-1} in the transfer reaction

$$\mathrm{HA}_{(\mathrm{dioxane})} + \mathrm{H}^+_{(\mathrm{aq.})} + \mathrm{A}^-_{(\mathrm{aq.})} \rightleftharpoons \mathrm{HA}_{(\mathrm{aq.})} + \mathrm{H}^+_{(\mathrm{dioxane})} + \mathrm{A}^-_{(\mathrm{dioxane})}$$

and this results in a change of 2.41 cal mole^{-1} in entropy.

Δpk_a^T(S–W) values, i.e., pK_a^T(S) – pK_a^T(W) (where S and W refer to mixed solvents and water, respectively) of thiovioluric acids at 30°C are given in Table 4. The change in pK_a^T(S–W) which is found to be different for the different acids for the same percentage of dioxane is probably due to the presence of different substituents which cause a great change in the distribution of electron density in the ring, and hence the electron density at any particular point is also affected.

ACKNOWLEDGEMENTS

Thanks are due to the Department of Chemistry, University of Roorkee, and Sahu Jain College, Najibabad, for providing the necessary facilities. One of the authors (V.K.B.) is grateful to UGC, New Delhi, for Senior Research Fellowship.

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