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Thermodynamics of acid proton dissociation of 5-hydroxy-1,4-naphthoquinone in dioxane–water mixtures

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Abstract

Thermodynamic proton–ligand dissociation constants ${}^{T}pK_a$ of 5-hydroxy-1,4-naphthoquinone (HHNQ) have been determined pH-metrically in 40–70 vol.% dioxane–water mixtures at 25 and 35 ± 0.1°C applying an empirical pH correction for mixed hydro-organic media. HHNQ is a weak monoprotic acid with ${}^{T}pK_a$ between 9.7 and 11.8. Values of ${}^{T}pK_a$ do not vary linearly with the reciprocal of the dielectric constant of the medium, but a plot of ${}^{T}pK_a$ versus the mole fraction of dioxane (n_2) is linear at a given temperature. The "true constant" K_a' and solvation number n in the expression $(H^+)(A^-)/(HA) = K_a'(S)^n = K_a^*$, have been evaluated by analysing the experimental data mathematically. Values of the changes in the standard free energy, enthalpy and entropy associated with its proton-ligand ionization have also been calculated. Positive values of $\Delta H^{\ominus}$ found in aqueous–dioxane media for HHNQ indicate the endothermicity of the proton ionization reactions. Temperature and media effects are briefly discussed.

1. INTRODUCTION

Hydroxynaphthoquinones and related compounds, with an anionic functionality (–OH) and a carbonyl group as coordinating site, possess varied medicinal, analytical and commercial applications [1,2]. Some interesting applications of this family of reagents include the photometric and gravimetric determinations of Th(IV), U(VI), Zr(IV) and tervalent lanthanum [3]. Of them, 5-hydroxy-1,4-naphthoquinone (HHNQ), commonly known as juglone, a tannin present in walnut kernels, is an important derivative. Analytical applications of this compound have been examined extensively in recent years [4,5].

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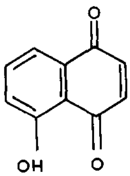
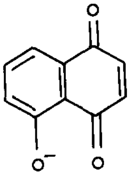


(keto)



(enol)

Juglone is a weak monoprotic acid. The proximity of the carbonyl and hydroxyl groups in this compound permits the formation of stable metal chelates with a large number of metal ions [6]. In comparison, few data for its enolization seem to have been reported so far. Most of the work to date, has, however, been restricted to the evaluation of its stoichiometric acid dissociation constant for some specific set of conditions. No value of the thermodynamic equilibrium constant for its ionization has been published, except in one instance [7] which concerns with pK_a values for juglone and other analogous hydroxyquinones in a 75% dioxane–water mixture at 30°C. This led us to a detailed study of the proton dissociation reactions of this ligand and to arrive at theoretically comparable thermodynamic data. In recent years, considerable effort has been put into the quantitative description and assessment of the effect of substituents, particularly on the physical properties such as ionization constants and on the reactivities of organic molecules. As a consequence, it is now possible to evaluate the thermodynamic proton-ligand ionization constants of organic acids with sufficient precision and accuracy, which has hitherto been rather difficult. The thermodynamic functions ($\Delta G^{\ominus}$, $\Delta H^{\ominus}$, $\Delta S^{\ominus}$) associated with the ionization of HHNQ are computed following the standard equations. The values of the solvation number and the true dissociation constants are also evaluated.

HHNQ is sparingly soluble in water; therefore, dioxane–water mixed media had to be used in the ${}^{T}pK_a$ determinations. In addition, the determination in binary mixed media also provides useful data for the theoretical understanding of the dissociation process in a system where two dipoles, for example dioxane and water, as well as the anion compete for the proton. The dioxane–water system is a good model because it covers a wide range of dielectric constants (from 78 to 2.2 for pure dioxane) and it consists of a polar, hydrogen-bonding component and a relatively non-polar component.

EXPERIMENTAL

Reagents

HHNQ, procured from Tokyo Chemical Industry Co, Japan, was used as supplied. An aqueous solution (10%) of tetramethylammonium hydroxide

(TMAH) titrant was standardized against potassium hydrogen phthalate and diluted to 0.1 M, the proportions of dioxane and water being the same as used in preparing the titre solutions. *p*-Dioxane was purified as recommended [8].

All other chemicals used were of AnalaR or G.R. Grade.

Apparatus

A Beckman Research pH-meter with a glass combination electrode, Orion model 91-02, was used for pH measurements; it can read up to 0.002 pH units. It was standardized with phthalate and borax buffers before and after each titration. A constant temperature was maintained (to an accuracy of ± 0.1°C) by circulating water from the thermostat, model Colora K-4661 (F.R.G.) through the annular space of a double-walled titration vessel.

Titration procedure

The titration procedure for determining ${}^{T}\mathrm{p}K_a$ was essentially the same as that outlined by Albert and Serjeant [9]. Normally, a 0.01 M reagent solution was titrated without the addition of inert salt. 47.5 ml of the appropriate dioxane–water mixture containing 0.01 M HHNQ was introduced into a thermostated (25 or 35 ± 0.1°C) titration vessel equipped with a magnetic stirring bar, a glass combination electrode and a microburette of 5.0 ml capacity. This initial volume of the titre solution was taken to allow for the change in total volume of solution on titrant addition [9]. For practical purposes, the error caused by volume correction is almost negligible (less than 0.01 pH unit for the central five readings of the titration set, with a maximum error of 0.018 pH unit [10]). After 10 min, the titration was started by adding 0.2 ml aliquots of 0.1 M TMAH and recording the highest stable pH value. Further titrant additions were made in the same manner. Titrations, conducted in duplicate, were reproducible to within ± 0.01 pH unit.

CALCULATIONS

Two methods were followed to calculate the ${}^{T}\mathrm{p}K_a$ values of this ligand: the non-logarithmic (N) and the logarithmic (L). A Norsk–Data computer was used for calculations.

Non-logarithmic method

The thermodynamic acid dissociation constant, ${}^{T}K_a$(aq) of an acid in an aqueous medium can be written as

$$ {}^{T}K_a(\mathrm{aq}) = [\mathrm{H}^+][\mathrm{A}^-]\Gamma^2 \pm /[\mathrm{HA}] \qquad (1) $$

where $\Gamma\pm$ is the mean activity coefficient. The activity coefficient of the neutral molecule HA is assumed to be unity. Also, we know that

$$[\mathrm{HA}] = [\mathrm{C_a}] - [\mathrm{A}^-] \tag{2}$$

where $[\mathrm{C_a}]$ denotes the total concentration of the acid. Substituting the value of [HA] from eqn. (2) into eqn. (1) and rearranging, we get

$$[\mathrm{A}^-] = -1/{}^{T}K_{\mathrm{a}}(\mathrm{aq})([\mathrm{A}^-][\mathrm{H}^+]\Gamma^2\pm) + [\mathrm{C_a}] \tag{3}$$

which is a straight-line equation $(y = mx + C)$ having slope m and intercept C equal to $-1/{}^{T}K_{\mathrm{a}}(\mathrm{aq})$ and $[\mathrm{C_a}]$ respectively, where $x = ([\mathrm{A}^-][\mathrm{H}^+] \times \Gamma_{\pm}^2)$ and $y = [\mathrm{A}^-]$. The least-squares method was used to evaluate the slope and intercept given by the above equation. Values of $[\mathrm{A}^-]$ and $[\mathrm{H}^+]$ were obtained analytically. The relationship of Van Uitert and Haas [10] was used to evaluate the hydrogen ion concentration from the values read on the pH-meter (B) in an aqueous dioxane medium

$$-\log[\mathrm{H}^+] = B + \log U_{\mathrm{H}}^{\ominus} - \log(1/\Gamma\pm)$$

Values of the correction factor, $\log U_{\mathrm{H}}^{\ominus}$, were obtained experimentally [11] and those of the mean activity coefficients, $\Gamma\pm$, were computed by interpolation of the data given by Harned and Owen [12] assuming that the mean activity coefficients are the same on both molal and molar scales.

Logarithmic method

Values of ${}^{T}\mathrm{p}K_{\mathrm{a}}$ in aqueous dioxane were calculated using the equation

$${}^{T}\mathrm{p}K_{\mathrm{a}} = B + \log U_{\mathrm{H}}^{\ominus} + \log([\mathrm{HA}]/[\mathrm{A}^-]) + \log(1/\Gamma\pm)$$

Details relating to the logarithmic method (L) of the computations are essentially the same as given elsewhere [13].

The thermodynamic functions $(\Delta G^{\ominus}, \Delta H^{\ominus}, \Delta S^{\ominus})$ associated with the acid dissociation were calculated using the standard equations

$$\Delta G^{\ominus}(25°\mathrm{C}) = 5.71\mathrm{p}K_{\mathrm{a}}(25°\mathrm{C})(\mathrm{kJ}) \tag{4}$$

$$\Delta G^{\ominus}(35°\mathrm{C}) = 5.90\mathrm{p}K_{\mathrm{a}}(35°\mathrm{C})(\mathrm{kJ}) \tag{5}$$

$$\Delta H^{\ominus} = 176.06[\mathrm{p}K_{\mathrm{a}}(25°\mathrm{C}) - \mathrm{p}K_{\mathrm{a}}(35°\mathrm{C})](\mathrm{kJ}) \tag{6}$$

$$-\Delta S^{\ominus}(25°\mathrm{C}) = 14.04[\Delta G^{\ominus}(25°\mathrm{C}) - \Delta H^{\ominus}](\mathrm{kJ}) \tag{7}$$

$$-\Delta S^{\ominus}(35°\mathrm{C}) = 13.58[\Delta G^{\ominus}(35°\mathrm{C}) - \Delta \mathrm{H}^{\ominus}](\mathrm{kJ}) \tag{8}$$

RESULTS AND DISCUSSION

Values of ${}^{T}\mathrm{p}K_{\mathrm{a}}$ for HHNQ obtained in different dioxane–water mixtures at 25 and 35°C are summarized in Table 1. These constants decreased

TABLE 1

Thermodynamic proton–ligand ionization constant of HHNQ

Vol. % dioxane	Mole fraction of dioxane (n_2)	${}^{T}pK_a$ at 25°C			${}^{T}pK_a$ at 35°C		
		Method L[a]	Method N[a]	Graph	Method L[a]	Method N[a]	Graph
40	0.123	9.94	9.86	9.86	9.78	9.66	9.66
50	0.174	10.37	10.22	10.30	10.20	10.00	10.11
60	0.240	11.28	10.94	10.94	11.18	10.80	10.80
70	0.330	12.41	11.78	11.78	12.33	11.67	11.67

[a] ${}^{T}pK_a$ values obtained using at least ten values of a titration set.

slightly with increasing temperature, which is to be expected because the enol content increases with rise in temperature [14]. Method N is superior to method L because the former does not involve the total concentration term. Furthermore, the accuracy of this method depends on the ability of the pH-meter to read correctly. Hence, the values obtained by the non-logarithmic method are used for all other detailed calculations and the plots. The ${}^{T}pK_a$ values are plotted against $(1/D_s - 1/D_w)$ (D_s = dielectric constant of the solvent, D_W = dielectric constant of water) (Fig. 1) and the mole fraction of dioxane, n_2 (Fig. 2). The empirical relations derived therefrom are given in Table 2. Similar relationships between ${}^{T}pK_a$ and n_2 were also calculated by subjecting the ${}^{T}pK_a$ data to least-squares analysis

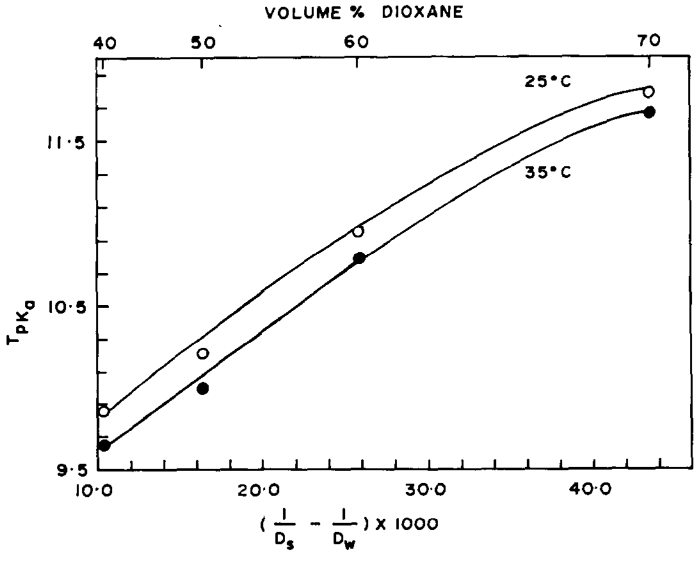


Fig. 1. Variation of ${}^{T}pK_a$ with the dielectric constant D of the medium.

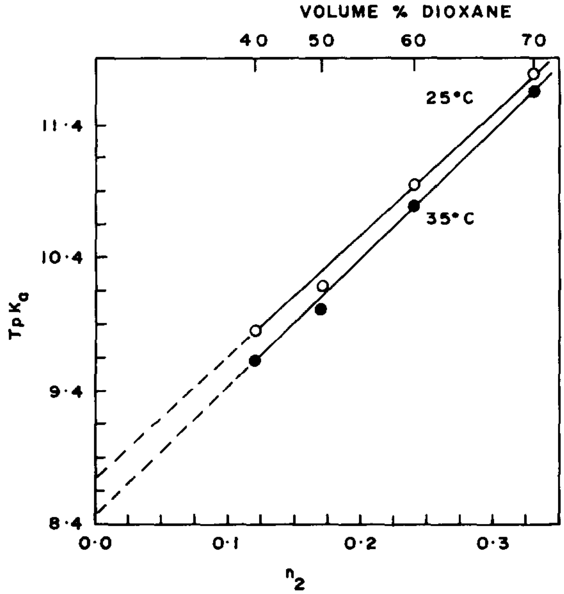


Fig. 2. Variation of ${}^{T}\mathrm{p}K_a$ with n_2 (mole fraction of dioxane).

(Table 2). Table 3 records the thermodynamic functions $\Delta G^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ computed by the temperature variation method.

Medium effect

The acid strength and thus, the ${}^{T}\mathrm{p}K_a$ values of monoprotonic acids are influenced by the intrinsic basicity of the solvent. When the dissociation of an acid gives a net increase of ions

$$\mathrm{HA} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{A^-}$$

a decrease in the dielectric constant of the solvent enhances the electro-

TABLE 2

Empirical relation between ${}^{T}\mathrm{p}K_a$ and n_2 of dioxane for HHNQ

${}^{T}\mathrm{p}K_a = mn_2 + C$, at 25°C				${}^{T}\mathrm{p}K_a = mn_2 + C$, at 35°C			
Graph		Least-squares		Graph		Least-squares	
m	C	m	C	m	C	m	C
9.22	8.74	9.09	8.73	9.65	8.49	9.52	8.47
Correlation coefficient		r	0.998			0.997	
Regression coefficient (actual slope)		b	9.22			9.65	

TABLE 3

Free energy, enthalpy and entropy changes for ionization of HHNQ

Function [a]	Solvent medium (vol.% dioxane)			
	40	50	60	70
$\Delta G^{\ominus}$ (25°)	56.30	58.39	62.50	67.23
$\Delta G^{\ominus}$ (35°)	57.01	59.02	63.75	68.90
$\Delta H^{\ominus} = 29.36$				
$-\Delta S^{\ominus}$ (25°)	0.19	0.20	0.21	0.23
$-\Delta S^{\ominus}$ (35°)	0.19	0.19	0.21	0.22

[a] $\Delta G^{\ominus}$ and $\Delta H^{\ominus}$ in kJ mol^{-1}; $\Delta S^{\ominus}$ in kJ K^{-1} mol^{-1}.

static forces between the oppositely charged ions and, thus, facilitates the formation of molecular species of the undissociated acid [15] which should increase the ${}^{T}\mathrm{p}K_a$, as seen for HHNQ in Table 1.

Sagar et al. [16] have proposed that the free energy of ionization of acids in solution at infinite dilution might be expressed as the sum of the electrostatic term (el), sensitive to the environment, and a non-electrostatic term (non), insensitive to the environment and independent of temperature. Thus

$$\Delta G^{\ominus}_{\mathrm{diss}} = \Delta G^{\ominus}_{\mathrm{el}} + \Delta G^{\ominus}_{\mathrm{non}} \tag{9}$$

If the electrostatic part is expressed by Born's formula [17], it follows that

$$\Delta G^{\ominus}_{\mathrm{el}} = -(Ne^2/2)(1 - 1/D)(1/r^+ + 1/r^-) \tag{10}$$

where r^+ and r^- denote the radii of the solvated ions and D the dielectric constant of the medium. Hence for the simultaneous transfer of the ions from water to an aquo-organic mixed medium, eqn. (9) takes the form

$$\Delta G^{\ominus}_{\mathrm{diss}} = \Delta G^{\ominus}_{\mathrm{non}} - (Ne^2/2)(1/D_s - 1/D_w)(1/r^+ + 1/r^-) \tag{11}$$

where D_s and D_w are the dielectric constants of the mixed medium and pure water, respectively. Further, because $\Delta G^{\ominus}_{\mathrm{diss}} = 2.303RT\mathrm{p}K_a$, the equation simplifies as

$$\mathrm{p}K_a = (\Delta G^{\ominus}_{\mathrm{non}}/2.303RT) - (Ne^2/4.606RT)(1/D_s - 1/D_w)(1/r^+ + 1/r^-) \tag{12}$$

Conventionally, $\mathrm{p}K_a$ is plotted against $1/D$ assuming that $\Delta G^{\ominus}_{\mathrm{non}}$ is independent of the solvent and that terms $(1/r^+ + 1/r^-)$ and $1/D_w$ are constant. Both types of relationships, namely, linear for water-rich media ($D_s > 30$) [18,19] and non-linear [20], have been reported. The plots of ${}^{T}\mathrm{p}K_a$ as a function of $(1/D_s - 1/D_w)$ for HHNQ do not obey a strict linear relationship: the plots possess distinct curvature (Fig. 1).

Mole fraction of dioxane

Direct participation of the solvent in the acid proton dissociation should provide a better understanding of the compositions of the mixed solvent as well as of the ionic solvates. For example, such a participation is quite evident from the straight line plot of $\mathrm{p}K_\mathrm{a}$ versus n_2 in several instances [21].

For HHNQ, the change in $^T\mathrm{p}K_\mathrm{a}$ with n_2 is of considerable magnitude. On altering the mole fraction of dioxane, an appreciable change in the $^T\mathrm{p}K_\mathrm{a}$ values is observed. When $^T\mathrm{p}K_\mathrm{a}$ values of HHNQ are plotted against n_2, linear relationships are obtained (Fig. 2). The plots gave slopes equivalent to about 10 which is as expected for diketones [22–24]. The fit was judged by calculating the correlation coefficient r [13]. Linear proportionality between the two variables is quite evident from the values of r which are approximately unity (Table 2). Likewise, linear proportionality is obtained for other mixed aqueous solvents, e.g. acetic, propionic, butyric and benzoic acids in methanol–water mixtures [25] and dimedone in ethanol–water [26].

Evaluation of pK$_a$ and n

The acid dissociation constant K_a' of an acid HA in a mixed medium can be expressed as

$$n\mathrm{S} + \mathrm{HA} \overset{K_\mathrm{a}'}{=} x\mathrm{SH}^+ + y\mathrm{SA}^- \tag{13}$$

where n is the total of x plus y moles of solvent S, aqueous dioxane being the medium in the present study. Hence

$$(x\mathrm{SH}^+)(y\mathrm{SA}^-)/(\mathrm{S})^n(\mathrm{HA}) = K_\mathrm{a}' \tag{14}$$

where the parentheses denote activity. Equation (14) is usually written as

$$(\mathrm{H}^+)(\mathrm{A}^-)/(\mathrm{HA}) = K_a'(\mathrm{S})^n = K_\mathrm{a}^* \tag{15}$$

where it is understood that the ions are solvated and K_a^* includes the solvent terms $(\mathrm{S})^n$. Taking logarithms of eqn. (15) gives

$$\log K_\mathrm{a}^* = \log K_\mathrm{a}' + n \log(\mathrm{S})$$

or

$$\mathrm{p}K_\mathrm{a}^* = \mathrm{p}K_a' - n \log(\mathrm{S}) \tag{16}$$

Because $\mathrm{p}K_\mathrm{a}^*$, defined in eqn. (16), is the thermodynamic constant, the $\mathrm{p}K_\mathrm{a}'$ value thus evaluated should be a true constant independent of the media, provided that the assumptions for S and n are correct.

Finally, the solvation number n can be computed from the following equation derived from eqn. (16)

$$n = [\mathrm{p}K_{\mathrm{a}2}^* - \mathrm{p}K_{\mathrm{a}1}^*]/[\log(\mathrm{S}_1) - \log(\mathrm{S}_2)]$$

TABLE 4

Calculation of true constant pK'_a for HHNQ [a]

Vol.% dioxane	pK_a^* (found)	Log(S)	pK'_a	pK_a^* (calc.)	pK_a^* (graph)
40	9.86	1.490	17.06	9.84	9.82
	9.66	1.488	17.16	9.64	9.60
50	10.22	1.394	16.96	10.31	10.30
	10.00	1.392	17.02	10.13	10.11
60	10.94	1.270	17.08	10.91	10.91
	10.80	1.269	17.20	10.75	10.76
70	11.78	1.097	17.07	11.74	11.77
	11.67	1.096	17.20	11.62	11.67

[a] First and second row values at 25°C and 35°C, respectively. At 25°C, $n = 4.87$ (calc.); 4.98 (graph): p$K'_a = 17.04$ (calc.); 17.23 (graph). At 35°C, $n = 5.06$ (calc.); 5.29 (graph): p$K'_a =$ 17.15 (calc.); 17.47 (graph).

The pK'_a and n values listed in Table 4 have been computed from the least-squares fitting of eqn. (16) and have also been obtained from a plot of pK_a^* (or ^{T}pK_a) against log(S) (Fig. 3). Graphical values show some deviation from the experimental ones. It is of interest to note that there is an excellent agreement between the two sets of values of ^{T}pK_a calculated independently using eqns. (3) and (16).

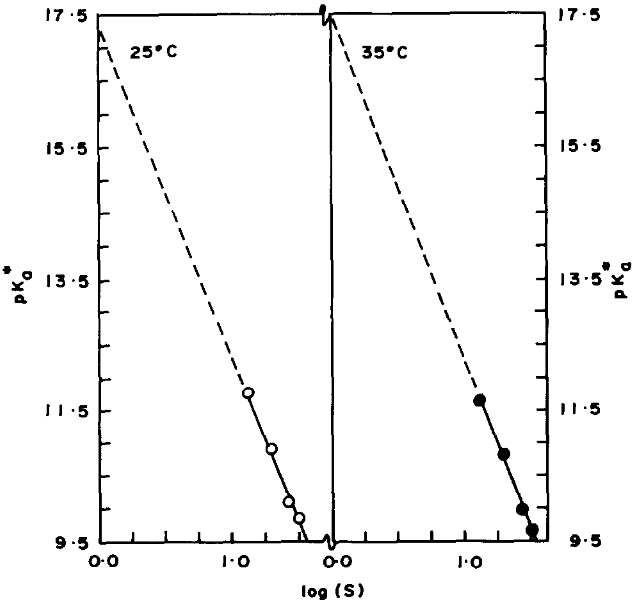


Fig. 3. Plots of pK_a^* versus log(S).

Thermodynamic functions of ionization

The ${}^{T}\mathrm{p}K_a$ values have been determined with a precision of $\pm 0.02 - \pm 0.03$ and, hence, the error in $\Delta G^{\ominus}$ is estimated to be between ± 0.13 and ± 0.17 kJ mol^{-1}. The procedure followed here to evaluate $\Delta H^{\ominus}$ is subject to some error because the enthalpy change is small and because the ${}^{T}\mathrm{p}K_a$ values were not obtained at several temperatures which would have allowed use of a more precise method [27]. However, the positive value of $\Delta H^{\ominus}$ found in dioxane–water solutions for HHNQ indicates that its ionization is accompanied by absorption of heat and the process is endothermic. Furthermore, the change in $\Delta H^{\ominus}$ with change in medium is relatively small and within experimental error. It is because of this that the slopes of the straight lines in the plot of ${}^{T}\mathrm{p}K_a$ versus n_2 (Fig. 2) are approximately the same at both temperatures (Table 2) and the two lines are parallel. It is therefore justifiable to assume that $\Delta H^{\ominus}$ is independent of solvent media over the range investigated. On this basis, a new value of $\Delta H^{\ominus}$ was calculated. Numerically, this is equal to 176.06 times the difference in the intercepts of the parallel lines on the ${}^{T}\mathrm{p}K_a$ axis (Fig. 2) and it is this value that is given in Table 3. The $\Delta S^{\ominus}$ values at different percentages of dioxane are found to be practically the same, thereby showing that it is independent of solvent composition.

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REFERENCES

1 I.H. Suffet and W.C. Purdy, J. Electroanal. Chem., 11 (1966) 302.
2 K.D. Jain, A.K. Jain, S.S. Sawhney and R.K. Sharma, J. Indian Chem. Soc., 52 (1975) 270, 552, 1101.
3 B.D. Jain and S.P. Singhal, Current Sci., 31 (1962) 279.
4 S.S. Sawhney and B.M.L. Bhatia, J. Indian Chem. Soc., 57 (1980) 438.
5 S.S. Sawhney and N.C. Trehan, Indian J. Chem., 14A (1976) 295.
6 B.M.L. Bhatia, S.D. Matta and S.S. Sawhney, Thermochim. Acta, 47 (1981) 367.
7 H. Kido, W.C. Fernelius and C.G. Haas, Anal. Chim. Acta, 23 (1960) 116.
8 A. Weissberger and E.S. Proskauer, Organic Solvents, Vol. 7, Interscience, New York, 1955, p. 139.
9 A. Albert and E.P. Serjeant, The Determination of Ionization Constant: A Laboratory Manual, 3rd edn., Chapman & Hall, London, 1984, pp. 14, 26.
10 L.G. Van Uitert and C.G. Haas, J. Am. Chem. Soc., 75 (1953) 451.
11 J.P. Shukla and S.G. Tandon, J. Electroanal. Chem., 35 (1972) 423.
12 H.S. Harned and B.B. Owen, The Physical Chemistry of Electrolytic Solutions, 3rd edn., Reinhold, New York, 1967, p. 716.

13 J.P. Shukla and R.S. Sharma, Electrochim. Acta, 31 (1986) 1449.
14 D.W. Thomson and A.L. Alfred, J. Phys. Chem., 75 (1971) 433.
15 M. Guilio, Electrochemistry, Principle, Practice and Application, Elsevier, Amsterdam, 1963, p. 80.
16 E.E. Sagar, R.A. Robinson and R.G. Bates, J. Res. Natl. Bur. Stand. Sect. A, 68 (1964) 305.
17 M.Z. Born, Z. Phys., 1 (1920) 45.
18 R.G. Bates, in B. Pesce (Ed.), Electrolytes, Pergamon Press, London, 1962, p. 196.
19 T. Shedlovsky, in B. Pesce (Ed.), Electrolytes, Pergamon Press, London, 1962, p. 146.
20 E.J. King, Acid–Base Equilibria, Pergamon, Oxford, 1965, p. 256.
21 H.S. Harned and B.B. Owen, The Physical Chemistry of Electrolytic Solutions, 3rd edn., Reinhold, New York, 1967, p. 756.
22 J.P. Shukla, V.K. Manchanda and M.S. Subramanian, J. Electroanal. Chem., 40 (1977) 431.
23 J.P. Shukla and M.S. Subramanian, Thermochim. Acta, 35 (1980) 293.
24 J.P. Shukla, A.K. Sabnis and M.S. Subramanian, Thermochim. Acta, 49 (1981) 361.
25 R.A. Robinson and R.H. Stokes, Electrolytic Solutions, Butterworth, London, 1955, Table 7, p. 541.
26 R.G. Bates and G. Schwarzenbach, Helv. Chim. Acta, 38 (1955) 699.
27 J. Lewis and R.G. Wilkins, Modern Coordination Chemistry, Interscience, New York, 1960, p. 18.