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THERMODYNAMICS OF THE DISSOCIATIONS OF *ORTHO*-, *META*-, AND *PARA*-AMINOBENZENE SULPHONIC, GLUTAMIC AND SULPHAMIC ACIDS IN FORMAMIDE AT DIFFERENT TEMPERATURES

UPENDRA N. DASH

Department of Chemistry, G.M. College, Sambalpur, Orissa (India)

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ABSTRACT

The thermodynamic dissociation constants of orthanilic, metanilic, sulphanilic, glutamic and sulphamic acids in formamide have been determined from 5 to 45°C at intervals of 5°C. Electromotive force measurements in cells without liquid junction (using quinhydrone and silver—silver chloride electrodes) were made. The thermodynamic quantities associated with the ionization of these amino acids have been calculated. These quantities are discussed in relation to the structure of the acid and the orientation of formamide molecules by the ions.

INTRODUCTION

In a previous communication [1], the pK values and associated thermodynamic quantities for the two dissociation steps of *ortho*-, *meta*-, and *para*-aminobenzoic acids, ampholytes, in formamide were reported. The first dissociation step is an acid—base equilibrium of the charge type $A^{+}B^{\pm}$, while the second is of the charge type $A^{\pm}B^{-}$. The effect of changing the solvent from water to formamide for the two dissociation steps of these ampholytes has also been examined. To extend the study on the behaviour of ampholytes, we now report the results of a determination of the pK values and associated thermodynamic constants for the dissociation steps of orthanilic, metanilic, sulphanilic, glutamic and sulphamic acids in formamide at nine different temperatures from 5 to 45°C. A comparison of these values of pK and their associated thermodynamic quantities (ΔG^0, ΔH^0, and ΔS^0) in both water and formamide helps to explain the dipolar character of these acids in formamide.

EXPERIMENTAL

Orthanilic, metanilic, glutamic and sulphamic acids (C.P.'s) were recrystallized twice from hot conductivity water, and sulphanilic acid (B.D.H., L.R.) was recrystallized twice from boiling conductivity water, and were dried at room temperature over calcium chloride in a vacuum desiccator. Hydrochlo-

rides of the amino acids were prepared by the method similar to that described earlier [1]. The purity of these acids was checked by titrations against a carbonate-free sodium hydroxide solution.

Potassium salts of these acids were prepared by the method as described earlier [2,4]. The purification of formamide and drying of KCl (B.D.H., AnalaR) have been described previously [4,5].

The detailed description of the apparatus, preparation of the electrodes, design of the cells, preparation of the cell solutions and cell measurements have been discussed previously [3]. The reproducibility of the result was about ±0.2 mV.

RESULTS

The pK_1 of orthanilic, metanilic, sulphanilic, and glutamic acids corresponds to the reaction represented by

$$HZ^+(\text{zwitterion}) = H^+ + Z^\pm \qquad (1)$$

where K_1 is the first ionization constant, and was determined in formamide by accurately measuring the EMF of cells of the type

$$Ag—AgCl|HZCl(m_2),\quad Z^\pm(m_1),\quad QH_2—Q|Pt \qquad (A)$$

The second ionization constant (K_2) of these acids and the K of sulphamic acid were found from measurements of the EMF of cells of the type

$$Ag—AgCl|KCl(m_3),\quad KZ(m_2),\quad Z^\pm(m_1),\quad QH_2—Q|Pt \qquad (B)$$

whereas, the third ionization constant of glutamic acid (K_3) was obtained by using a cell of the type

$$Ag—AgCl|KCl(m_3),\quad K_2Z(m_2),\quad KHZ(m_1),\quad QH_2—Q|Pt \qquad (C)$$

where m_1, m_2, and m_3 are the stoichiometric molalities of each of the species involved. The method used was very similar to the EMF procedure employed earlier [1,2]. Quinhydrone electrodes have been used instead of hydrogen electrodes [3].

The EMF of cell (A) was measured with different solutions for each acid ranging from $m_1 = 0.224$ and $m_2 = 0.048$ up to $m_1 = 1.198$ and $m_2 = 1.164 \times 10^{-2}$ mol kg^{-1}. For the solutions of cell (B), m_1, m_2, and m_3 were varied in the ranges 0.132—1.028, 0.110—2.784, and 1.196—9.945 × 10^{-2} mol kg^{-1}, respectively. Similarly, the EMF of cell (C) was measured with different solutions ranging from $m_1 = 0.686$, $m_2 = 0.211$ and $m_3 = 1.438$ up to $m_1 = 1.978$, $m_2 = 1.452$ and $m_3 = 13.041 \times 10^{-2}$ mol kg^{-1}.

The "apparent" pK_1 of orthanilic, metanilic, sulphanilic and glutamic acids, designated pK_1', was derived from the EMF, E, of cell (A), and the molalities of the cell solutions by the equation [1,6]

$$pK_1' = (XF/2.303RT) + \log[m_2(m_2 - m_H')/m_1 + m_H')] - 2A(Id_0)^{1/2}/1 + Ba(Id_0)^{1/2} \qquad (2)$$

and the 'apparent' hydrogen ion molality, m'_H was calculated by

$$-\log m'_H = (XF/2.303\,RT) + \log m_2 - 2A(Id_0)^{1/2}/1 + Ba(Id_0)^{1/2} \quad (3)$$

where $X = [E - E^0(\text{Ag—AgCl}) + E^0(\text{QH}_2\text{—Q})]$, and "$a$" is the ion-size parameter. The Debye—Hückel constants A and B at different temperatures were available in the literature [7] or were calculated from the dielectric constant [8], density [9], etc. of formamide. The standard electrode potentials, E^0, of the silver—silver chloride and quinhydrone electrodes in formamide at different temperatures are available elsewhere [10]. The ionic strength, I, is equal to the molality, m_2, in the solutions of cell (A). As before [11,12], the value of "a" for each acid was obtained. A linear extrapolation of pK'_1 to $I = 0$ gave the pK_1 values of the acids.

The second ionization constants, pK_2, of orthanilic, metanilic, and sulphanilic acids, and the ionization constant, pK, of sulphamic acid were obtained by linear extrapolation to zero ionic strength, $I = 0$, of the "apparent" pK_2, designated pK'_2 (pK and pK', respectively, for sulphamic acid) defined by the equation [4]

$$pK'_2 = [2A(Id_0)^{1/2}/1 + Ba(Id_0)^{1/2}] - \log[m'_H(m_2 + m'_H)/(m_1 - m'_H)] \quad (4)$$

where m'_H is the "apparent" hydrogen ion molality related to the EMF, E, of cell (B) through the relation [4]

$$-\log m'_H = (XF/2.303\,RT) + \log m_3 - 2A(Id_0)^{1/2}/1 + Ba(Id_0)^{1/2} \quad (5)$$

The ionic strength of the solutions of cell (B) for these acids is given by

$$I = m_2 + m_3 + m'_H \quad (6)$$

As the hydrogen ion molality is negligible compared to m_1 and m_2 in the case of the second ionization constant of glutamic acid, the following more simple equation was used [4]

$$pK'_2 = (XF/2.303\,RT) + \log(m_1 m_3/m_2) \quad (7)$$

The ionic strength of the solutions of glutamic acid of cell (B) is given by

$$I = m_2 + m_3 \quad (8)$$

As expected, pK'_2 varied linearly with I at each temperature; the intercept at $I = 0$ is the value of pK_2.

Similarly, pK_3 was obtained from the EMF of cell (C) by the extrapolation to $I = 0$ of the "apparent" values of pK'_3 given by [2]

$$pK'_3 = (XF/2.303\,RT) + \log(m_1 m_3/m_2) + 2A(Id_0)^{1/2}/1 + Ba(Id_0)^{1/2} \quad (9)$$

The ionic strength of the solutions of cell (C) is given by

$$I = m_1 + 3m_2 + m_3 \quad (10)$$

The values of pK, pK_1, pK_2 and pK_3 for the acids thus obtained are listed in Table 1, together with their standard deviations. The standard deviations were calculated by the method of least-squares fit of the point to a straight line for each acid at different temperatures. The values of ΔG^0, ΔH^0 and ΔS^0 evaluated [1] at 25°C are presented in Table 2, along with their standard deviations.

TABLE 1

Ionization constants (pK) of sulphamic, orthanilic, metanilic, sulphanilic and glutamic acids in formamide at different temperatures (± denotes the standard deviation of the intercept)

Acid		Temp. (°C)								
		5	10	15	20	25	30	35	40	45
Sulphamic	pK	2.05 ± 0.05	2.01 ± 0.05	2.14 ± 0.02	2.12 ± 0.04	2.44 ± 0.08	2.27 ± 0.07	2.12 ± 0.05	2.02 ± 0.001	2.00 ± 0.02
Orthanilic	pK_1	2.39 ± 0.04	2.33 ± 0.06	2.32 ± 0.05	2.22 ± 0.03	1.99 ± 0.05	2.08 ± 0.01	1.93 ± 0.02	1.89 ± 0.01	1.93 ± 0.02
	pK_2	3.48 ± 0.03	3.49 ± 0.04	3.37 ± 0.03	3.23 ± 0.03	3.36 ± 0.01	3.26 ± 0.03	3.40 ± 0.02	3.26 ± 0.04	3.21 ± 0.01
Metanilic	pK_1	1.98 ± 0.03	1.99 ± 0.03	1.86 ± 0.01	1.80 ± 0.02	1.71 ± 0.03	1.64 ± 0.02	1.48 ± 0.03	1.44 ± 0.05	1.12 ± 0.08
	pK_2	4.37 ± 0.01	4.41 ± 0.02	4.42 ± 0.02	4.32 ± 0.005	4.36 ± 0.03	4.24 ± 0.01	4.22 ± 0.01	4.19 ± 0.02	4.17 ± 0.02
Sulphanilic	pK_1	2.04 ± 0.03	1.97 ± 0.01	1.95 ± 0.01	1.82 ± 0.02	1.81 ± 0.05	1.77 ± 0.05	1.69 ± 0.07	1.65 ± 0.03	1.56 ± 0.06
	pK_2	3.91 ± 0.08	3.98 ± 0.08	3.88 ± 0.08	3.96 ± 0.08	3.88 ± 0.08	3.98 ± 0.08	3.998 ± 0.07	3.999 ± 0.08	3.992 ± 0.08
Glutamic	pK_1	4.05 ± 0.08	3.98 ± 0.08	3.86 ± 0.04	3.94 ± 0.08	3.89 ± 0.08	3.73 ± 0.03	3.43 ± 0.04	3.39 ± 0.04	3.37 ± 0.03
	pK_2	6.38 ± 0.01	6.34 ± 0.01	6.24 ± 0.01	6.18 ± 0.02	5.96 ± 0.08	5.95 ± 0.06	5.95 ± 0.03	5.94 ± 0.01	5.86 ± 0.01
	pK_3	10.25 0.01	10.35 ± 0.04	10.10 ± 0.02	10.12 ± 0.04	9.91 ± 0.03	9.66 ± 0.01	9.56 ± 0.04	9.35 ± 0.01	9.24 ± 0.04

TABLE 2

Values of pK and thermodynamic functions for the ionization of orthanilic, metanilic, sulphanilic, sulphamic, glutamic, and glutaric acids in formamide and water at 25°C (± denotes the standard deviation)

Acid	pK	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1} deg^{-1})
	First ionization step			
Orthanilic	1.99	11.35 ± 0.20	23.15 ± 0.08	39.55 ± 0.38
Metanilic	1.71	9.76 ± 0.12	33.85 ± 0.05	80.82 ± 0.26
	0.39 *	2.23 *		
Sulphanilic	1.81	10.33 ± 0.20	19.48 ± 0.08	30.70 ± 0.38
	0.58 *	3.31 *		
Glutamic	3.89	22.19 ± 0.32	31.17 ± 0.16	30.13 ± 0.78
	2.162 *	12.34 *	−0.27 *	−42.26 *
	Second ionization step			
Orthanilic	3.36	19.18 ± 0.05	9.57 ± 0.02	−32.24 ± 0.12
	2.46 *	14.02 *	9.93 *	−13.72 *
Metanilic	4.35	24.828 ± 0.12	10.88 ± 0.05	−46.79 ± 0.26
	3.74 *	21.73 *	19.41 *	−7.95 *
Sulphanilic	3.88	22.14 ± 0.32	−3.56 ± 0.16	−86.25 ± 0.78
	3.23 *	15.43 *	17.57 *	−2.93 *
Sulphamic	2.44	13.92 ± 0.32	−0.16 ± 0.01	−47.26 ± 0.78
	0.988 *	5.64	1.97 *	−12.55 *
Glutamic	5.96	34.00 ± 0.32	23.27 ± 0.16	−36.01 ± 0.78
	4.272 *	24.37 *	1.56 *	−76.57 *
Glutaric	6.22	35.46	30.84	−15.50
	Third ionization step			
Glutamic	9.91	56.54 ± 0.12	48.18 ± 0.05	−28.07 ± 0.26
	9.358 *	53.39 *	40.07 *	−44.77 *
Glutaric	8.21	46.81	30.80	−53.73

* From ref. 16.

TABLE 3

Relative amounts (K_z) of zwitterion and neutral molecule coexisting in formamide for orthanilic, metanilic, sulphanilic and glutamic acids

T (°C)	Orthanilic	Metanilic	Sulphanilic	Glutamic
15.	11.22	362.97	85.13	239.83
25	23.44	436.53	117.53	117.52
		2236 *	443 *	128.83 *
35	29.52	489.72	203.18	331.11
45	19.06	1122.02	270.26	309.13

* Value calculated in water.

TABLE 4

Estimated values of r (Å) of glutamic and glutaric acids in formamide at different temperatures

Acid	Temp. (°C)								
	5	10	15	20	25	30	35	40	45
Glutamic	0.687	0.658	0.688	0.649	0.671 0.699 *	0.724	0.750	0.806	0.818
Glutaric					1.62				

* Value calculated in water.

The relative amounts K_z of zwitterion and neutral molecule coexisting in the solution for orthanilic, metanilic, sulphanilic and glutamic acids calculated at 25°C by the equation [13]

$$K_z = [HZ_+]/[Z_+] = K_1/K_2 \quad (11)$$

are presented in Table 3 along with the values calculated in water.

The distance r(Å) between the carboxylic groups of glutamic acid was calculated from the Bjerrum equation as described earlier [3,10]. The values have been presented in Table 4 with that of glutaric acid in formamide [2].

DISCUSSION

The effect of temperature on the pK values of acids shown in Table 1 is consistent with the behaviour of other acids studied in formamide [1,2,10, 14]. As apparent in Table 2, the higher values of pK in formamide than in water [14,15] are in agreement with the general behaviour shown by weak acids in solvents of this class [1,4,10,14]. Comparing the pK_1 and pK_2 values of *ortho*-, *meta*-, and *para*-aminobenzene sulphonic acids in formamide with those available in water at 25°C, it is seen that these acids exhibit a similar order in their relative strengths in both formamide and water, pointing to the fact that the effect of the orientations on the strength of aminobenzene sulphonic acid is independent of the change of solvent.

A glance at the corresponding pK values of glutamic and glutaric acids (Table 2) reveals that the alterations of acidic strength for both ionization steps brought about by amino substitution in glutaric acid are possibly to be attributed both to $+I$ and $+T$ effects of the amino group which is electron-donating in nature as it has a weak $+I$ effect, and a strong $+T$ effect. Enhancement of acidic strength in the second ionization step of glutamic acid in comparison with the first ionization of glutaric acid is probably due to the stabilization of monoglutamate anion by intramolecular hydrogen bonding between the far end carboxylate ion and the amino group. The change in pK_3 is more pronounced than in pK_2 in the case of glutamic acid as compared with the pK_2 of glutaric acid. The decrease in acidic strength in

the third ionization of glutamic acid might be due to the transmission of the electrostatic effect of the negative charge of the monoglutamate ion to the centre of ionization at the remaining carboxylic group through the carbon chain through hydrogen bonding [3].

The values of the ion-size parameter, a, of the acids, orthanilic (4 Å), metanilic (4 Å), sulphanilic (4 Å), glutamic (6 Å), glutaric (6 Å) and sulphamic (5 Å) in formamide show that the amino substituent at the *ortho*-, *meta*-, and *para*-positions of the benzene sulphonic acids and at the α-position of glutaric acid has no effect on the a values of the acids. This is consistent with the *ortho*-, *meta*-, and *para*-substituted aminobenzoic acids.

From Table 2, it is evident that the increase in ΔG^0 values from the first to the second or from the second to the third ionization step in formamide is due to an increase in the electrostatic free energies of the ions generated by the second or the third dissociation process of the corresponding acid. The increase in ΔG^0 on passing from water to formamide may be due to the fact that the acids are more solvated in formamide than in water. The change in ΔH^0 values for the different ionization steps of the acids in formamide or in changing the solvent from water to formamide indicates that the solvation pattern of the acids is not only altered significantly for different ionization steps but also for the change of solvent. It is of further interest to compare the results of the standard entropies of ionization for the acids in both formamide and water (Table 2). The more negative values of ΔS^0 in formamide than in water point to the fact that the degree of reorientation and partial immobilization of the formamide molecules by the acids is greater in formamide than in water, while the reverse occurs in the case of the higher ΔS^0 values in formamide.

It is of interest to examine the relative amounts of the zwitterion in formamide and to compare the results in both formamide and water. From Table 3, it is seen that as the K_z values increase the dipolar character of the acids increases in formamide with increase of temperature. As compared with the values in water (Table 3), it is evident that these ampholytes represent a mixture, in the structural sense, of the predominant neutral molecule species with a small portion of the dipolar species in formamide in comparison with that in water. However, in both solvents, the dipolar character of *o*-, *m*-, and *p*-aminobenzene sulphonic acids increases in the order *meta* > *para* > *ortho*.

As is apparent from Table 4, the values of r for glutamic acid show an irregularity with change of temperature. A comparison of the values of r in both formamide and water at 25°C shows the failure of the Bjerrum equation which is consistent with the behaviour of other acids studied in formamide [3,10]. Comparing the value of r of glutamic acid with that of glutaric acid in formamide, it is seen that the amino substituent at the α-position of glutaric acid decreases the distance between the carboxyl groups, supporting the view that the third ionization constant of glutamic acid is depressed more than the second in comparison with the corresponding ionization constant of glutaric acid [3].

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