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BEHAVIOUR OF AMPHOLYTES IN FORMAMIDE

I. THE IONIZATION CONSTANTS AND RELATED THERMODYNAMIC QUANTITIES OF *o*-, *m*-, AND *p*-AMINOBENZOIC ACIDS AT DIFFERENT TEMPERATURES

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ABSTRACT

The ionization constants of *ortho*-, *meta*-, and *para*-aminobenzoic acids have been determined, in formamide, at different temperatures ranging from 5 to 45°C, using cells without liquid junction potential. From the values of the ionization constants of these acids, thermodynamic parameters associated with the ionization processes of these acids have been evaluated.

INTRODUCTION

No work seems to have been done on the study of the behaviour of ampholytes in formamide, a solvent closely resembling water from the standpoint of dielectric constant and viscosity. The present work deals with similar studies on the behaviour of the ampholytes, such as, *ortho*-, *meta*-, and *para*-aminobenzoic acids in formamide. The first ionization constants of these acids have been determined in this solvent at the temperatures ranging from 5 to 45°C using the cells of type,

$$\text{Pt, } H_2|HZ(m_1), \text{ HZHCl}(m_2)|AgCl\text{–}Ag \qquad (A)$$

where HZ stands for the *o*-, *m*-, or *p*-aminobenzoic acid, and HZHCl for its hydrochloride.

The second ionization constants of these acids have been reported in formamide[1] over this temperature range using the cells of type,

$$\text{Pt, } H_2|HZ(m_1), \text{ KZ}(m_2), \text{ KCl}(m_3)|AgCl\text{–}Ag \qquad (B)$$

From the values of the first and second ionization constants of these acids, the existence, in the structural sense, of these acids in formamide medium has been investigated.

EXPERIMENTAL

The aminobenzoic acids (B.D.H., L.R.) were recrystallized thrice from hot water after decolourising the solutions with active charcoal. Hydrochlorides of these

TABLE 1

DETERMINATION OF $-\log K_{1a}$ OF AMINOBENZOIC ACIDS IN FORMAMIDE AT 25°C
$M = [m_2(m_2 - m(H^+))/(m_1 + m(H^+))]$

$10^3 m_1$ (mol kg^{-1})	$10^3 m_2$ (mol kg^{-1})	E (V)	$\frac{(E-E^\circ)F}{2.303\,RT}$	$10^4 m(H^+)$ (mol kg^{-1})	$-\log M$	$2A\sqrt{\mu d_0}$	$10^3 \mu$	$-\log K'_{1a}$
o-Aminobenzoic acid								
0.601	0.096	0.6086	6.934	1.271	3.8851	0.0202	0.096	3.0287
0.256	0.133	0.5776	6.409	3.096	3.3254	0.0238	0.133	3.0598
0.405	0.198	0.5586	6.088	4.409	3.1683	0.0290	0.198	2.8907
0.458	0.456	0.5189	5.417	9.292	2.5221	0.0441	0.456	2.8508
0.660	0.654	0.4985	5.072	14.630	2.3853	0.0528	0.654	2.6339
0.718	0.703	0.4996	5.091	13.080	2.3245	0.0547	0.703	2.7118
0.620	0.821	0.4867	4.873	18.690	2.1905	0.0591	0.821	2.6234
0.999	0.993	0.4799	4.757	20.480	2.1872	0.0650	0.993	2.5048
							$-\log K_{1a}$ (extrapolated) = 3.08 ± 0.08	
m-Aminobenzoic acid								
0.455	0.116	0.6290	7.280	0.476	3.5520	0.0222	0.116	3.6958
0.684	0.158	0.6175	7.084	0.554	3.4566	0.0259	0.158	3.6015
0.280	0.196	0.5798	6.446	1.953	2.9374	0.0289	0.196	3.4797
0.568	0.439	0.5592	6.098	2.007	2.5049	0.0432	0.439	3.5499
0.929	0.638	0.5498	5.939	2.033	2.3818	0.0521	0.638	3.5051
0.902	0.898	0.5286	5.581	3.369	2.0811	0.0618	0.898	3.4381
1.158	0.998	0.5276	5.564	3.178	2.0913	0.0652	0.998	3.4075
							$-\log K_{1a}$ (extrapolated) = 3.64 ± 0.04	
p-Aminobenzoic acid								
0.445	0.079	0.5920	6.653	2.936	4.0840	0.0183	0.079	2.5507
0.456	0.133	0.5625	6.155	5.558	3.6963	0.0238	0.133	2.4349
0.290	0.195	0.5375	5.732	10.160	3.3348	0.0288	0.195	2.3684
0.554	0.199	0.5395	5.765	9.226	3.4819	0.0291	0.199	2.2540
2.014	1.085	0.4630	4.472	36.390	2.4829	0.0680	1.085	1.9211
1.439	1.470	0.4494	4.241	46.880	2.1128	0.0791	1.470	2.0491
2.926	1.558	0.4584	4.394	31.260	2.2227	0.0814	1.558	2.0899
4.898	2.636	0.4328	3.961	52.970	1.9902	0.1059	2.636	1.8649
							$-\log K_{1a}$ (extrapolated) = 2.41 ± 0.08	

acids were prepared by passing hydrochloric acid gas, obtained from concentrated sulphuric acid and sodium chloride (B.D.H., AnalaRs) into the hot aqueous solutions of the corresponding amino acids. The needle-shaped crystals of the hydrochlorides of these acids thus obtained on cooling, were further recrystallized from hot water after decolourising with active charcoal. The crystals, in each case were dried in a bottle through which dry, purified air was passed. The purity of these acids was checked by titrations against a carbonate-free sodium hydroxide solution. Formamide was purified as described in our earlier article[2].

Solutions for e.m.f. measurements for the cell (A) were prepared by dissolving appropriate weighed amounts of acids and acid hydrochlorides in known weights of formamide.

Cell measurements were carried out with electrodes prepared in the same manner as those used by Agarwal and Nayak[3].

RESULTS AND DISCUSSION

The results of the e.m.f. measurements for cell (A) for aminobenzoic acids at 25°C together with other data are presented in Table 1. Similar experimental values were obtained at each of the 5°C temperature intervals throughout the range.

The first ionization reaction of the aminobenzoic acids may be represented by[4]

$$HZH^+ \rightleftharpoons HZ + H^+$$

and accordingly, the first ionization constant, K_{1a} by

$$K_{1a} = \frac{m(HZ)\cdot m(H^+)}{m(HZH^+)} \cdot \frac{\gamma(HZ)\cdot\gamma(H^+)}{\gamma(HZH^+)}$$

where HZ represents the neutral-molecule structure of aminobenzoic acid, and m and γ are the molalities and the activity coefficients of the species designated in parentheses.

The e.m.f., E, of the cell

$$Pt, H_2|HZ(m_1).\ HZHCl(m_2)|AgCl\text{-}Ag \qquad (A)$$

is given by eqn (1) as suggested by Harned and Owen[4] for ampholytes.

$$\frac{(E-E^\circ)^F}{2.303\,RT} + \log\frac{m(Cl^-)m(HZH^+)}{m(HZ)} + \log\frac{\gamma(Cl^-)\gamma(HZH^+)}{\gamma(HZ)} - \log K_{1a} \qquad (1)$$

Expressing the activity coefficients by the limiting law, eqn (1) leads to an extrapolation function, K'_{1a}

$$\frac{(E-E^\circ)^F}{2.303\,RT} + \log\frac{m(Cl^-)m(HZH^+)}{m(HZ)} - 2A(\mu d_0)^{1/2} = -\log K'_{1a} \qquad (2)$$

Since $m(Cl^-) = m_2$, $m(HZ) = m_1 + m(H^+)$, and $m(HZH^+) = m_2 - m(H^+)$, the middle term in the left-hand side of eqn (2) can be calculated from the experimental values of m_1 and m_2 and that of $m(H^+)$ as obtained from eqn (3)

$$-\log m(H^+) = \frac{(E-E^\circ)^F}{2.303\,RT} + \log m(Cl^-) - 2A(\mu d_0)^{1/2} \tag{3}$$

where the ionic strength, μ is given by

$$\mu = m_2$$

The values of E°(Ag–AgCl) and d_0 needed for the calculations at different temperatures in formamide were obtained from the empirical equations available in the literature[5,6]. The values of the Debye–Huckel contant, A, were either obtained from the literature[7] or calculated in the molal scale by the usual method using the exact values of density, dielectric constant[8], etc., of the solvent, formamide for different temperatures. The values of $\log K'_{1a}$ thus calculated were found to vary linearly[9,10] with μ at different temperatures and the linear extrapolation to zero

TABLE 2

VALUES FOR pK_{1a} OF *o*-, *m*-, AND *p*-AMINOBENZOIC ACIDS IN FORMAMIDE AT DIFFERENT TEMPERATURES

Benzoic acid	*Temperature (°C)*								
	5	*10*	*15*	*20*	*25*	*30*	*35*	*40*	*45*
o-Amino	3.70± 0.08	3.53± 0.04	3.52± 0.08	3.33± 0.09	3.08± 0.08	2.86± 0.08	3.07± 0.08	3.36± 0.09	3.28± 0.09
m-Amino	3.89± 0.08	3.59± 0.01	3.64± 0.02	3.61± 0.04	3.64± 0.04	3.66± 0.09	3.51± 0.08	3.51± 0.09	3.36± 0.09
p-Amino	2.94± 0.08	2.55± 0.09	2.58± 0.08	2.40± 0.08	2.41± 0.08	2.49± 0.08	3.03± 0.09	2.86± 0.08	3.18± 0.09

TABLE 3

VALUES OF THE EXPERIMENTAL SLOPES OF THE STRAIGHT LINES OF BEST FIT FOR THE ACIDS AT DIFFERENT TEMPERATURES

Temp. (°C)	*Slope ($V\,mol^{-1}\,kg^{-1}$)$\times 10^{-2}$*		
	o-Amino	*m-Amino*	*p-Amino*
5	−0.552	−0.540	−0.532
10	−0.232	−0.408	−0.422
15	−0.551	−0.107	−0.508
20	−0.628	−0.222	−0.359
25	−0.577	−0.223	−0.234
30	−0.316	−0.808	−0.760
35	−0.340	−0.720	−0.679
40	−0.618	−0.715	−0.739
45	−0.708	−0.890	−1.063

ionic strength of the values of log K'_{1a} yields log K_{1a} at the corresponding temperatures. Extrapolation of log K'_{1a} to corresponding zero ionic strength was done by the method of least squares. Values of pK_{1a} for the aminobenzoic acids are shown in Table 2 along with their accuracies. Values of the slopes of the straight line of best fit for each acid at different temperatures are found to be negative and are presented in Table 3.

A comparison of the present data with the corresponding values in water is difficult because of the lack of relevant data in water at all temperatures. However, available data at 25°C in water[11] (the pK_a values for these acids in formamide at all temperatures are presented in Table 4 along with those in water at 25°C) show that the pK_a values are higher in formamide than in water, which is in agreement with a general behaviour shown by weak acids in solvents of this class[5,9,10]. Comparing the pK_{1a} and pK_{2a} values for these acids in water and formamide, it is found that in changing the solvent from water to formamide, the second ionization constants of these acids are depressed more than the first, pointing to the fact that the ampholytes behave in a manner similar to that of the dicarboxylic acids in formamide[5,10,12] with respect to their second ionization process.

TABLE 4

VALUES OF pK_{1a} AND pK_{2a} FOR *o*-, *m*-, AND *p*-AMINOBENZOIC ACIDS IN FORMAMIDE AT DIFFERENT TEMPERATURES

Temp. (°C)	pK_{1a}			pK_{2a}		
	o-Amino	*m-Amino*	*p-Amino*	*o-Amino*	*m-Amino*	*p-Amino*
5	3.70	3.89	2.94	7.07	6.60	7.51
10	3.53	3.59	2.55	6.97	6.83	7.45
15	3.52	3.64	2.58	6.85	6.89	7.27
20	3.33	3.61	2.40	7.05	6.65	7.45
25	3.08	3.64	2.41	6.65	6.42	6.94
30	2.86	3.66	2.49	6.65	6.35	7.14
35	3.07	3.51	3.03	6.55	6.28	7.08
40	3.36	3.51	2.86	6.39	6.22	6.99
45	3.28	3.36	3.18	6.54	6.36	6.97

Increase of temperature has a general effect of lowering the pK_{1a} values of these acids. However, irregularities are noticed at higher temperatures for which there is no ready explanation. These might be due to structural changes occurring in the hydrogen bonded solvent with the change of temperature. Assuming the heat of ionization to be constant over the entire temperature range, the ΔH_1° values for the first ionization of these acids have been evaluated from the slopes of the plots of log K_{1a} against $1/T$. The standard free energy change, ΔG_1° for the ionization process of the acids is obtained from the relation, $\Delta G_1^\circ = -RT \ln K_{1a}$ and the standard entropy change, ΔS_1° is evaluated from the relation, $\Delta S_1^\circ = (\Delta H_1^\circ - \Delta G_1^\circ)/T$. These values are presented in Table 5 along with those for the second ionization process evaluated in formamide[1] at 25°C for the sake of comparison.

TABLE 5

THERMODYNAMIC QUANTITIES FOR AMINOBENZOIC ACIDS IN FORMAMIDE AT 25°C

Benzoic acid	$\Delta G_1^\circ \times 10^{-3}$ (J)	$\Delta G_2^\circ \times 10^{-3}$ (J)	$\Delta H_1^\circ \times 10^{-3}$ (J)	$\Delta H_2^\circ \times 10^{-3}$ (J)	ΔS_1° (J deg^{-1})	$\Delta S_2^\circ \times 10^{3}$ (J deg^{-1})
o-Amino	17.57	37.93	20.24	35.04	8.96	−9.70
m-Amino	20.77	36.63	24.13	27.53	11.28	−30.54
p-Amino	13.81	39.62	−8.77	29.62	−75.77	−33.56

ΔG_1° and ΔG_2° values are both positive indicating that ionization is not spontaneous in the two processes. The positive values of ΔH_1° in cases of *ortho* and *meta*, and that of ΔH_2° in *ortho*, and *para* acids show that the reaction is endothermic, in the first and second ionization processes, respectively, where the negative values of ΔH_1° suggest the reaction to be exothermic in the first ionization of *para*-aminobenzoic acid. The negative values of ΔS_1° for *para*, and that of ΔS_2° for *ortho*, *meta*, and *para* acids indicate that there is more order in the ionized form than in the unionized form in the corresponding ionization processes of these acids, while the reverse is the case in the first ionization processes of *ortho*-, and *meta*-aminobenzoic acids because of their positive ΔS_1° values. Considering these facts, it is expected that *para*-aminobenzoic acid behaves in a different manner in formamide in comparison with the *ortho* and *meta* acids.

It is of interest to examine the effect of the orientations on the strength of aminobenzoic acid in formamide medium and to compare it with that in water. Considering the pK_{1a} and pK_{2a} values for the *ortho*-, *meta*-, and *para*-aminobenzoic acids at 25°C, their strengths appear in the order

meta	>	*ortho*	>	*para*
3.64		3.08		2.41

and

meta	<	*ortho*	<	*para*
6.42		6.65		6.95

in formamide and

meta	>	*para*	>	*ortho*
3.12		2.41		2.11

and

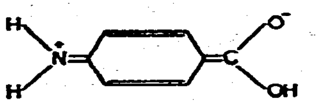
meta	<	*para*	<	*ortho*
4.74		4.85		4.95

in water, for the pK_{1a} and pK_{2a} values, respectively.

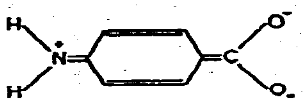
It is interesting to note a reverse order of the $\mathrm{p}K_{1a}$ and the $\mathrm{p}K_{2a}$ values in both formamide and water medium at 25°C. The tabulated $\mathrm{p}K_{1a}$ and $\mathrm{p}K_{2a}$ values for these acids in formamide seem to indicate that these trends actually exist over the temperature range employed, 5 to 45°C.

The order of the strength of *ortho*-, and *para*-aminobenzoic acids is found to be different in formamide from that in water. This discrepancy is reasonable, since formamide despite its high dielectric constant is less basic than water. The amino substituent in the *ortho* position increases the basicity of the acid by a factor of 4.5 in formamide, while an amino group in the *para* position enhances the basicity only by a factor of 2.5 in water medium. In *para*-aminobenzoic acid the decrease in hydrogen ion affinity, or basicity, in formamide, may be due to the fact that the acid undergoing dissociation is in neutral form with a smaller portion of the dipolar species in this solvent than in water in comparison with the *ortho* substituent amino acid.

According to the qualitative theory, the amino substituent is expected to be electron donating in nature as it has a weak $+I$, effect and also a strong $+T$ effect, which stablizes the acid (a) more than its anion (b).

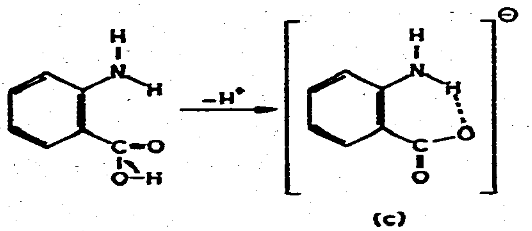


(a)



(b)

This effect is expected to be more from *ortho*, or *para* than from *meta* positions. Consequently, *o*- and *p*-aminobenzoic acids are expected to be weaker than *m*-aminobenzoic acid. The results in formamide amply support this view. However, between the *ortho* and *para* substituted amino benzoic acids, the *ortho* substituted acid is found to be stronger than the *para* substituted acid. This is probably again due to intramolecular hydrogen bonding as shown in (c) which partially compensates the $+I$ and $+T$ effects of the amino group stabilizing the anion



(c)

Klotz and Gruen[13] have shown that *p*-aminobenzoic acid exists in solution predominantly (91–97%) in the neutral molecule form. Deviney et al.[14] have also reported from the values of $\mathrm{p}K_{1a}$ and $\mathrm{p}K_{2a}$ for this acid, the existence of *p*-aminobenzoic acid in solution predominantly in the neutral molecule species with a small portion of the dipolar species. $\mathrm{p}K_{1a}$ and $\mathrm{p}K_{2a}$ as determined in formamide really represent a mixture, in the structural sense, of the predominant neutral molecule species with a small portion of the dipolar species. As the basicity increases, the dipolar character of the acids increases in the order, *meta*>*ortho*>*para* in formamide medium.

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