

## Thermodynamics of Ionization of Benzoic Acid in Urea + Water Mixtures

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Thermodynamic ionization constants ( ${}_sK_a$ ) of benzoic acid (HBz) have been determined from e.m.f. studies of the cell: Pt, H<sub>2</sub> (g, 1 atm)/HBz ( $m_1$ ), NaBz ( $m_2$ ), NaCl ( $m_3$ ), solvent/AgCl-Ag in aqueous solutions containing 11.52, 20.31, 29.64 and 36.83 wt % urea at 10°, 15°, 20°, 25° and 30°C. The related thermodynamic quantities, viz.  $\Delta G^\circ$ ,  $\Delta S^\circ$  and  $\Delta H^\circ$  have been evaluated and the solvent effects on these parameters discussed in the light of dielectric constant, specific solvation effects of the different species and the involved structural changes of the solvents.

IN course of our studies on the relative structuredness of aquo-organic solvents including urea + water mixtures, from the transfer energetics of various electrolytes<sup>1</sup> and non-electrolytes<sup>2</sup>, those of benzoic acid<sup>2b</sup> (HBz) also proved fairly useful. Although HBz was considered to serve as an essentially non-electrolyte in aqueous mixtures of methanol, ethanol and isopropanol because of decreasing dielectric constant, it could hardly be taken to do so in aqueous mixtures of urea for the increased dielectric constant ( $\epsilon$ ) resulting from the increasing proportion of urea<sup>3</sup>, is likely to increase the ionization of the acid. So, in order to account for the effect of enhanced ionization of HBz in aqueous urea solutions the knowledge of thermodynamics of ionization of HBz in urea-water mixtures is essential. We, therefore, report in this paper the ionization constant ( ${}_sK_a$ ) of the acid in aqueous solutions of urea containing 11.52, 20.31, 29.64 and 36.83% (by wt) of urea at 10°, 15°, 20°, 25° and 30° and the related thermodynamic quantities.

### Materials and Methods

Preparation of the solvents and the electrodes has been described earlier<sup>4</sup>. HBz and NaCl, both of Merck, GR variety, were used after usual pretreatment. The stock buffer solutions in each solvent were prepared by adding appropriate amounts of NaCl and HBz solutions to known amounts of standard NaOH solution. Concentrations in moles kg<sup>-1</sup> ( $m$ ) of all the components in the stock solutions were obtained by simple calculations. The stock solvents as well as the solutions were preserved at low temperature ( $\sim 5^\circ\text{C}$ ). Buffer solutions of different ionic strengths were prepared from the stock solutions by mass dilution.

General experimental procedures were similar to those described earlier<sup>1c,4</sup>. Constancy of the e.m.f. readings to  $\pm 0.2$  mV for 1 hr was considered the criterion of equilibrium. A Harned-Ehlers<sup>5</sup> type cell (A) was used.

Pt, H<sub>2</sub>(g, 1 atm)|HBz( $m_1$ ), NaBz( $m_2$ ), NaCl( $m_3$ ), solvent|AgCl-Ag

(A)

### Results

The  $p({}_sK_a)$  values of the acid in each of the solvents at different temperatures were determined adopting Harned and Owen's method<sup>6</sup> for the ionization constants of the order of  $10^{-4}$  or greater. Accordingly, the 'apparent' hydrogen ion concentrations ( $m'_{\text{H}^+}$ ) were computed directly from the e.m.f.'s ( $E$ ) corrected to 1 atm. H<sub>2</sub> pressure, for the respective buffer solutions by Eq. (1).

$$-\log m'_{\text{H}^+} = \frac{E - ({}_sE_m^\circ)_{\text{AgCl-Ag}}}{2.303 RT/F} + \log m_3 - 2S_f\sqrt{\mu'} \quad \dots(1)$$

where  $\mu' = (m_2 + m_3)d_s$  and  $S_f = 1.824 \times 10^6 (\epsilon T)^{-3/2}$ . The required values of the density ( $d_s$ ) of the solvents and  $S_f$  were obtained from an earlier paper<sup>4</sup>. The apparent ionization constants  $K'_a$  corresponding to  $m'_{\text{H}^+}$  values were obtained from the relation (2).

$$\log K'_a = \log \frac{m'_{\text{H}^+}(m_2 + m'_{\text{H}^+})}{m_1 - m'_{\text{H}^+}} - 2S_f (\mu d_s)^{1/2} \quad \dots(2)$$

where  $\mu = m_2 + m_3 + m'_{\text{H}^+}$ . The true  $p({}_sK_a)$  value at any temperature for a particular solvent was then obtained by extrapolating to  $\mu = 0$ , the observed linear plot of  $p({}_sK_a)$  (vide, Fig. 1, for a typical case) against  $\mu$ . The required values of  ${}_sE_{\text{AgCl-Ag}}^\circ$  at different temperatures for each of the solvents were taken from an earlier paper<sup>4</sup>. The values of  $p({}_sK_a)$  on molal scale thus obtained are presented in Table 1.

The  $p({}_sK_a)$  values at different temperatures for each of the solvents were fitted to Harned-Robinson type expression<sup>7</sup> (3)

$$p({}_sK_a) = A/T - B + CT \quad \dots(3)$$

by the method of least squares. The values of the coefficients  $A$ ,  $B$  and  $C$  for the solvents are given in Table 2. The values obtained using Eq. (3) are reproducible within  $\pm 0.005$  unit of the observed values. The values of the thermodynamic quantities, viz.  $\Delta G^\circ$ ,  $\Delta S^\circ$  and  $\Delta H^\circ$  (molal scale) for the ionization of the acid in the respective solvents were computed from the constants of the Eq. (3) and are given in Table 2.

In order to have a better understanding of the solvent effect, the changes of standard thermodynamic quantities ( $\Delta X^\circ = \Delta G^\circ$ ,  $\Delta S^\circ$  or  $\Delta H^\circ$ ) accompanying the ionization of the acid (HBz) in any solvent ( ${}_s\Delta X^\circ$ ) relative to that in pure water ( ${}_w\Delta X^\circ$ ) have been computed at 25° on mole fraction scale (N)<sup>8</sup> using Eq. (4).

$$\begin{aligned} \delta(\Delta X^\circ)_N &= ({}_s\Delta X^\circ)_N - ({}_w\Delta X^\circ)_N \\ &= ({}_s\bar{X}_{H^+}^\circ + {}_s\bar{X}_{Bz^-}^\circ - {}_s\bar{X}_{HBz}^\circ) \\ &\quad - ({}_w\bar{X}_{H^+}^\circ + {}_w\bar{X}_{Bz^-}^\circ - {}_w\bar{X}_{HBz}^\circ) \\ &= \Delta X_i^\circ(H^+) + \Delta X_i^\circ(Bz^-) - \Delta X_i^\circ(HBz) \end{aligned}$$

where  $\bar{X}_i^\circ$  is the standard partial molal thermodynamic parameter for the species  $i$  in the solvent concerned and  $\Delta X_i^\circ(i)$  represents the changes in the thermodynamic parameter accompanying the transfer of one mole of the species  $i$  from the standard state in water to the standard state in the solvent concerned, both on mole fraction scale. These values are listed in Table 3 and their variations with solvent composition are illustrated in Fig. 2.

### Discussion

As expected, the ionization of the acid increases with increased proportion of urea in water. But the magnitude of increase is not in accordance with Born's prediction<sup>9</sup> for the  $pK$  values pass through a minimum at 29.64 wt % urea, while the decrease in  $\epsilon^{-1}$  values is fairly monotonic<sup>5</sup>. Also, as is usual for many uncharged acids in many

solvents<sup>10,11</sup>, the variation of  $p({}_sK_a)$  values of this uncharged acid with temperature in any solvent mixture (Table 1) does not exhibit any maximum within this temperature range, which usually results from the opposing effects of increased thermal agitation and decreased dielectric constant with the rise in temperature. Moreover, the monotonic nature of  $\delta(\Delta G^\circ)$ -composition profile (Fig. 2) reflects that the solvent effect on the ionization is an involved process as is expected from the fact that it is guided by the resultant effects of free energy

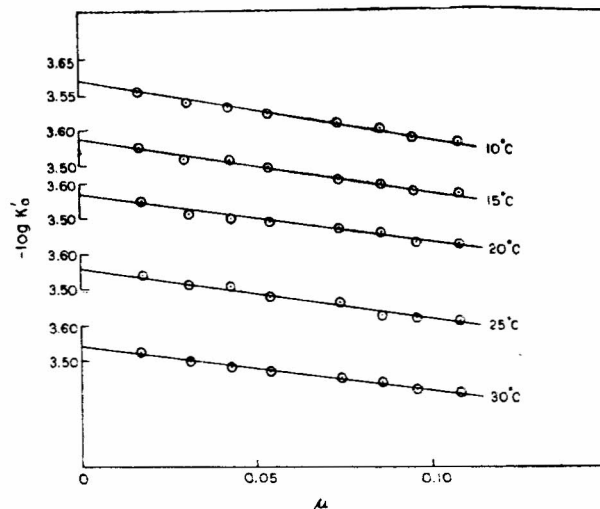


Fig. 1 — Typical extrapolation curves for evaluating  $p({}_sK_a)$  values of benzoic acid in 29.64 wt % urea-water mixture at different temperatures

TABLE 1 —  $p({}_sK_a)$  VALUES FOR THE IONIZATION OF BENZOIC ACID IN UREA-WATER MIXTURES AT DIFFERENT TEMPERATURES

| Wt % urea | $p({}_sK_a)$ * at |      |      |      |      |
|-----------|-------------------|------|------|------|------|
|           | 10°               | 15°  | 20°  | 25°  | 30°  |
| 11.52     | 3.93              | 3.93 | 3.92 | 3.91 | 3.90 |
| 20.31     | 3.83              | 3.82 | 3.81 | 3.80 | 3.78 |
| 29.64     | 3.59              | 3.58 | 3.57 | 3.56 | 3.54 |
| 36.83     | 3.78              | 3.77 | 3.76 | 3.74 | 3.72 |

\*Uncertainties in the  $p({}_sK_a)$  values are of the order of  $\pm 0.005$  unit.

TABLE 3 — VALUES OF  $\delta(\Delta G^\circ)$ ,  $T\delta(\Delta S^\circ)$  AND  $\delta(\Delta H^\circ)$  AT 25° FOR THE IONIZATION OF BENZOIC ACID IN UREA + WATER MIXTURES

| Wt % urea | [Values in kJ mol <sup>-1</sup> (mole fraction scale)] |                           |                          |                         |                         |                          |
|-----------|--|---------------------------|--------------------------|-------------------------|-------------------------|--------------------------|
|           | $\delta(\Delta G^\circ)$                               | $T\delta(\Delta S^\circ)$ | $\delta(\Delta H^\circ)$ | $\Delta G_i^\circ(HBz)$ | $\Delta G_i^\circ(H^+)$ | $\Delta G_i^\circ(Bz^-)$ |
| 11.52     | -1.88  | 5.28                      | 3.40                     | -0.92                   | -1.51                   | -1.29                    |
| 20.31     | -2.68  | 7.33                      | 4.65                     | -1.67                   | -2.89                   | -1.46                    |
| 29.64     | -4.23  | 8.71                      | 4.48                     | -2.45                   | -4.48                   | -2.20                    |
| 36.83     | -3.26  | 8.46                      | 5.20                     | -3.14                   | -5.90                   | -0.50                    |

TABLE 2 — COEFFICIENTS OF EQ. (3) AND  $\Delta G^\circ$ ,  $\Delta S^\circ$  AND  $\Delta H^\circ$  VALUES AT 25° FOR IONIZATION OF BENZOIC ACID IN UREA + WATER MIXTURES

| Wt % urea      | (Values in molal scale) |         |                   |  |  |  |
|----------------|-------------------------|---------|-------------------|--|--|--|
|                | A                       | B       | 10 <sup>2</sup> C | $\Delta G^\circ$<br>kJ mol <sup>-1</sup> | $\Delta S^\circ$<br>JK <sup>-1</sup> mol <sup>-1</sup> | $\Delta H^\circ$<br>kJ mol <sup>-1</sup> |
| 0 <sup>a</sup> | 819.6                   | 1.287   | 0.9190            | 23.97                                    | -80.3  | 0.03                                     |
| 11.52          | -1432.4                 | -14.106 | -1.8180           | 22.30                                    | -62.6  | 3.64                                     |
| 20.31          | -1451.6                 | -14.424 | -1.9308           | 21.67                                    | -55.7  | 5.06                                     |
| 29.64          | -1452.9                 | -14.191 | -1.9323           | 20.33                                    | -51.1  | 5.10                                     |
| 36.83          | -2192.7                 | -19.483 | -2.8127           | 21.34                                    | -51.9  | 5.86                                     |

(a) Ref. 8.

Assuming that the maximum uncertainty in  $p({}_sK_a)$  values in all the solvents is of the order  $\pm 0.005$ , the estimated [Please, N.W., *Biochem. J.*, 56 (1954), 196] maximum uncertainties in the values of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  at 25° are of the order:  $\pm 0.02$ ,  $\pm 1$  kJ mole<sup>-1</sup> and  $\pm 2$  JK<sup>-1</sup> mol<sup>-1</sup> respectively.

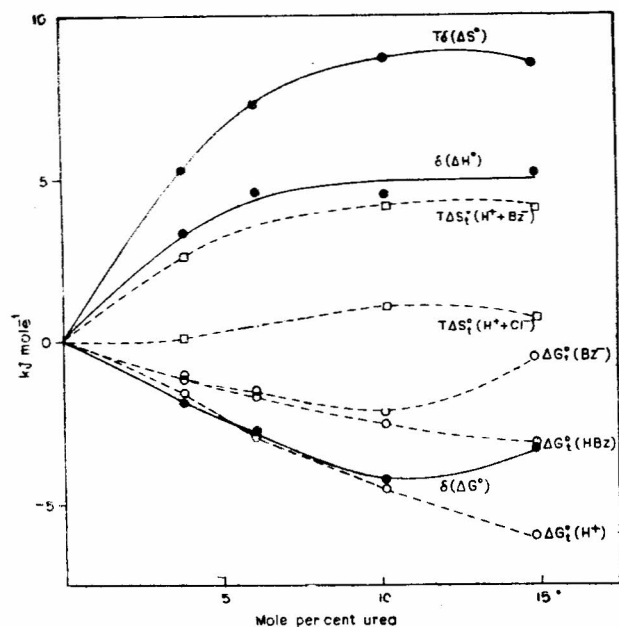
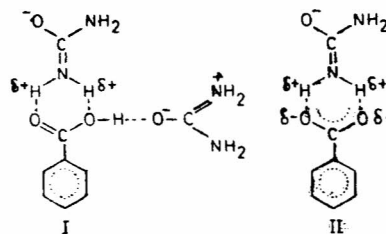


Fig. 2—Variation of solvent effects on thermodynamic quantities accompanying ionization of benzoic acid and transfer free energies of the species involved at 25° with mole % urea

transfer of the individual species involved in ionization [vide, Eq. (4)]. So, for a real understanding of the solvent effects on ionization of the benzoic acid the knowledge of the behaviour of individual species is in order. Since  $\Delta G_i^\circ$  values of HBz have recently been obtained from the measured solubilities of the acid in the solvents<sup>2b</sup>, and those of  $H^+$  from reference electrolyte ( $Ph_4AsBPh_4$ ) assumption<sup>12</sup>, these values were utilized to compute  $\Delta G_i^\circ$  values for  $Bz^-$  using Eq. (4). These values are listed in Table 3 along with those for  $H^+$  and HBz. The  $\Delta G_i^\circ$  (i)-composition profiles for the species are also illustrated in Fig. 2.

It is interesting to note that  $\Delta G_i^\circ$  ( $H^+$ ) values are increasingly negative as are expected from the effects of increased basicity<sup>10,4,13,14</sup> as well as increased dielectric constant of the solvents<sup>3</sup>. Also, the increased downward trend of  $\Delta G_i^\circ$  (HBz)-composition profile reflects increased solvation of the acid. As indicated earlier<sup>12</sup>, this possibly results from the 'acid-base' type interactions of the zwitterionic form  $\overset{+}{N}H_2=C(NH_2)-\overset{-}{O}$ —the actual contributor to the resonating structures of urea, with the  $-\text{COOH}$  group of the acid, as there is little scope of dispersion type interactions between the hydrophobic Ph-group and the zwitterionic form of urea. Moreover, the observed downward curve of  $\Delta G_i^\circ$ -profile of  $Bz^-$  which lies above that for HBz, indicates that the magnitude of increased solvation of  $Bz^-$  is less compared to HBz. This suggests that while the solvation of  $-\text{COOH}$  group of HBz is dictated by the 'acid-base' type interaction<sup>15,16</sup> as shown in structure (I), that for  $-\text{COO}^-$  of  $Bz^-$  is dictated by the 'acid-base' type interaction as shown in structure (II).

The observed upward trend of  $\Delta G_i^\circ$  ( $Bz^-$ ) beyond 10 mole % is possibly due to 'structural interaction'<sup>17</sup>



of the phenyl group at that structurally critical region of the mixed solvents<sup>10,4,18</sup>.

Solvent effects on the other thermodynamic parameters  $T\delta(\Delta S^\circ)$  and  $\delta(\Delta H^\circ)$ , accompanying the ionization of the acid, as reflected in their respective profiles shown in Fig. 2, are highly involved quantities. This is because both the parameters are dictated not only by the resulting effects of the transfer quantities of the individual species concerned, but each of which also is guided by the complex effects of structural changes of the solvents concerned<sup>18</sup>. Moreover, unlike  $\Delta G_i^\circ$  values,  $\Delta S_i^\circ$  and  $\Delta H_i^\circ$  values which are known for the neutral species HBz, those for  $H^+$  are not known. It is, therefore, difficult to separate the contribution of the individual species, without which any meaningful conclusion is hardly feasible.

However, interestingly enough, when  $T\Delta S_i^\circ(H^++Bz^-)$  values obtained by subtracting the corresponding values of  $HBz^{2b}$  from the values of  $T\delta(\Delta S^\circ)$  are plotted against composition, the resulting curve (Fig. 2) is found to be strikingly similar to that for  $(H^++Cl^-)$ <sup>4</sup>.

As indicated earlier<sup>4</sup> in the case of  $(H^++Cl^-)$ , the observed profile is dictated, partly by Born type electrostatic effect and partly by chemical effect<sup>9</sup>. The electrostatic effect when corrected at least tentatively by Born equation<sup>4</sup>, shifts the chemical part downward retaining the essential features almost unaltered. And the 'chemical part' has been shown to result from the effect of structural changes of the solvents<sup>4</sup>. Although proper correction for the electrostatic part of  $T(\Delta S_i^\circ)$  for  $(H^++Bz^-)$  is not feasible, it is expected that the chemical contribution will not be untowardly different from the total  $T\delta(\Delta S^\circ)$  or from the corresponding part for  $(H^++Cl^-)$ . It may, therefore, be concluded that the contribution of  $H^+$  being common, the observed difference in both the curves (Fig. 2) is likely to result from the hydrophobic structure promoting effect of Ph-group<sup>2b</sup> of  $Bz^-$ , which is pronounced in pure water but less so in the mixed solvents.

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