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# THERMODYNAMICS FOR THE IONIZATION OF BENZOIC ACID IN ETHANOL + WATER MIXTURES AT 298.1 K

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## ABSTRACT

The heat of neutralization of benzoic acid in water and ethanol + water mixtures (0–44 wt% of alcohol) have been determined calorimetrically. The enthalpies of ionization for the reaction

$HBz \rightleftharpoons H^+ + Bz^-$

were calculated using the values of heat of neutralization of benzoic acid and the enthalpies of ionization of water in mixed solvents. The free energy changes for the reaction were determined from solubility and pH measurements. The thermodynamics of transfer for the ionization of benzoic acid were coupled with the thermodynamics of transfer of $H^+$ ion and neutral benzoic acid to get the thermodynamics of transfer of benzoate ion. The results are interpreted in terms of structural changes of the solvent mixtures associated with the ionization of benzoic acid.

## INTRODUCTION

Studies on the effect of solvents on the dissociation constants of weak electrolytes have been comparatively wide but studies on the effect of solvents on the enthalpies of dissociation of weak electrolytes (acid or bases) are relatively few. It has been admitted, by and large, that the free energy of transfer does not represent the complex structural contributions associated with the dissociation of acids or bases due to known compensations of enthalpy and entropy of solvation [1]. The enthalpy of dissociation of a weak acid (like benzoic acid) represents the enthalpy changes due to the breaking of bonds as well as the complex structural contributions associated with the solvation of different species. The true nature of solvation is yet to be fully understood.

In order to explore the role of solvents on the thermodynamic properties of the weak acid, we have determined the enthalpy changes for the dissociation of benzoic acid

$$\underset{(HBz)}{C_6H_5COOH} \rightleftharpoons \underset{(Bz^-)}{C_6H_5COO^-} + H^+ \qquad (1)$$

in ethanol + water mixtures (0–44.0 wt% of alcohol).

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The $\Delta H^0$ values have been coupled with $\Delta G^0$ values of benzoic acid determined from solubility measurements to evaluate the entropy changes associated with the dissociation process which we present in this communication.

## EXPERIMENTAL

Ethanol was purified in the usual way [2,3]. The caustic soda pellets (G.R. E. Merck) were washed carefully with carbonate-free double-distilled water and finally dissolved in water. Benzoic acid (G.R., E. Merck) was recrystallized from alcohol + water mixtures and dried and kept in a desiccator. Perchloric acid (G.R., E. Merck) and other chemicals were estimated in the usual way. A description of the calorimeter has been given earlier [4,5].

A known amount of benzoic acid, dissolved in the appropriate solvent, was added to an excess of caustic soda solution in the same solvent to ensure complete neutralization of the benzoic acid. A blank experiment was performed for each set of measurements. The performance of the calorimeter was checked periodically using the determination of the heat of neutralization of caustic soda solution with perchloric acid.

For the determination of the dissociation constant of benzoic acid at 298.1 K, the solubility of benzoic acid was determined as described earlier [6,7] and the hydrogen ion concentrations of the saturated solutions of benzoic acid were measured using a Systronics digital pH meter.

## RESULTS

The heats of neutralization per mole of benzoic acid were calculated from the relation

$$\Delta H_{\mathrm{n}} = -\frac{Q}{C}\,\mathrm{kJ} \tag{2}$$

where $Q$ is the amount of heat evolved for the complete neutralization of $C$ gmol of benzoic acid. Since we have used a dilute solution of benzoic acid, the enthalpy changes have been assumed to be $\Delta H_{\mathrm{n}}^0$.

The enthalpies of ionization of benzoic acid ($\Delta H^0$) have been calculated from the values thus obtained and the heats of ionization of water ($\Delta H_{\mathrm{w}}^0$) in different mixed solvents interpolated from the data in the literature [8,9].

$$\Delta H^0 = \Delta H_{\mathrm{n}}^0 - \Delta H_{\mathrm{w}}^0 \tag{3}$$

The dissociation constant of benzoic acid at 298.1 K was determined from the relation

$$K_{\mathrm{T}} = \frac{C_{\mathrm{H}^+}^2}{C_{\mathrm{T}} - C_{\mathrm{H}^+}} \times f_{\pm}^2 = K \times f_{\pm}^2 \tag{4}$$

TABLE 1

Dissociation constants, heats of neutralization and the thermodynamics (in kJ mol$^{-1}$) of benzoic acid in ethanol–water mixtures

| Ethanol (wt%) | A | Total benzoic acid concentration $C_T$ (mol l$^{-1}$) | pH | p$K$ | p$K_T$ | Heat of neutralisation of benzoic acid | $\Delta G^0$ | $\Delta H^0$ | $-T\Delta S^0$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.0 | 0.509 | 0.0284 | 2.89 | 4.20 | 4.22 (±0.01) | 53.21 (±0.10) | 23.96 | 2.43 | 21.53 |
| 8.0 | 0.555 | 0.0389 | 2.88 | 4.33 | 4.37 (±0.01) | 55.94 (±0.30) | 24.93 | 0.70 | 24.17 |
| 16.4 | 0.613 | 0.0577 | 2.89 | 4.53 | 4.57 (±0.02) | 57.80 (±0.50) | 26.07 | −0.92 | 26.99 |
| 25.3 | 0.694 | 0.1201 | 2.87 | 4.81 | 4.86 (±0.02) | 52.80 (±0.30) | 27.72 | 3.20 | 24.53 |
| 34.4 | 0.791 | 0.3593 | 2.77 | 5.09 | 5.15 (±0.02) | 52.30 (±0.30) | 29.38 | 1.85 | 27.53 |
| 44.0 | 0.927 | 0.7785 | 2.69 | 5.27 | 5.35 (±0.02) | 44.39 (±0.40) | 30.52 | 5.93 | 24.59 |
| 54.1 | 1.133 | 1.3061 | 2.73 | 5.57 | 5.67 | | | | |
| 64.7 | 1.348 | 1.7316 | 2.83 | 5.90 | 6.00 | | | | |
| 76.0 | 1.707 | 2.2034 | 2.93 | 6.20 | 6.32 | | | | |
| 87.6 | 2.179 | 2.6656 | 3.02 | 6.46 | 6.59 | | | | |

where $C_T$ = total benzoic acid determined from solubility measurements, and $C_{H^+}$ = concentration of $H^+$ ion in the saturated solutions of benzoic acid determined pH-metrically.

Appropriate corrections were applied to the pH-meter readings to get the true $H^+$ ion concentrations in the mixed solvents [10,11]. The values of the activity coefficients of the ions were calculated using the Debye–Hückel limiting law.

The appropriate $A$ values in each solvent mixture were calculated from the known values of the dielectric constants of the ethanol + water mixtures interpolated from the values given by Akerlof and Short [12]. The results are shown in Table 1.

The heats of neutralization and the thermodynamics of ionization of benzoic acid ($\Delta G^0 = -2.303RT \log K$, $\Delta H^0$ and $\Delta S^0$) values are given in Table 1.

## DISCUSSION

The p$K$-values of benzoic acid determined from solubility measurements agree well with the values determined by us from conductometric measurements [13] except at two higher percentages where the differences are appreciable. But if we use the Davies equation [14], the values are closer. The agreement is good when we compare the p$K$-values reported by Grunwald and Berkowitz [15] and Panichajakul and Woolley [16] below 64 wt%, beyond which differences are considerable.

The enthalpy of neutralization of benzoic acid passes through an exothermic maximum at about 25 wt% of alcohol. The result is in accord with the enthalpy of ionization values of water reported by Hepler and co-workers [8,9] and Aditya et al. [17].

Hepler and co-workers [18,19] reviewed the thermodynamics of ionization of aqueous benzoic acid. The reported values of $\Delta H^0$ at 298 K range from $-420$ to $+169$ cal mol$^{-1}$. They consider $\Delta H^0 = +110$ cal mol$^{-1}$ to be the "best" value.

Our value of 2.43 kJ mol$^{-1}$ for the enthalpy of ionization of benzoic acid is comparatively higher than the value of 0.42 kJ mol$^{-1}$ reported by Hepler et al. [18,19]. But if we take 56.65 kJ mol$^{-1}$ as the heat of ionization of water, the value of $\Delta H^0$(HBz) comes out to be 1.59 kJ mol$^{-1}$. It is difficult to assign a reason for the difference. However, the value of Matsui et al. [19] is based on the differences of heats of solution of sodium benzoate in 0.001 M NaOH (A), and in 0.024–0.048 M HCl (B) at 298 K, whereas our value is based on the differences of heats of neutralization of benzoic acid and perchloric acid by caustic soda solutions. The different methods for obtaining $\Delta H^0$(HBz) may be the reasons for the difference. Moreover, since the value of $\Delta H^0$(HBz) invariably depends on the difference of two measured values, an uncertainty always exists.

It is seen that the dissociation is not favourable from both the enthalpic and entropic points of view. Dissociation creates charged ions which are responsible for the immobilization of the solvent molecules leading to a decrease in entropy. It is apparent that though the solubility of benzoic acid increases with the increase in organic solvent, the dissociation is not favoured for electrostatic reasons. The enthalpy and entropy of ionization of benzoic acid pass through a minimum at about 16 wt% of ethanol and a minimum is also observed at about 34 wt%.

The results cannot be ascribed to structural characteristics of aquo-organic solvent mixtures but reflect the structural rearrangement of water due to increasing addition of the co-solvent ethanol, together with the structural rearrangement arising from the solvation of $H^+$, $Bz^-$ and HBz. The thermodynamic changes due to the reaction $ROH + H_3O^+ \rightleftharpoons ROH_2^+ + H_2O$ may also make some contribution.

It is to be noted that the enthalpy changes were found to be maximal at about 20 wt% of alcohol in case of enthalpies of ionization of $Hphen^+$ or $Hbipy^+$ [3–5,17]. The results have been ascribed to enhancement of the three-dimensional structure of water with the addition of alcohol. The maximum structuration occurs around $X_2 = 0.1$ ($\sim$ 20 wt%) of alcohol [20]. The structure of water + ethanol mixtures is manifested in the complex concentration dependence of excess thermodynamic properties of mixing $\Delta H^E$ (exothermic maximum at $X_2 = 0.2$), $T\Delta S^E$ (negative maximum at $X_2 \simeq 0.3$) and $\Delta G^E$ (a maximum in the positive $\Delta G^E$ at $X_2 = 0.5$) where $X_2$ = mole fraction of alcohol [21].

Though it is extremely difficult to ascertain the contributions of the constituents to the thermodynamics of dissociation and thus get better insight regarding ion–solvent interactions, we have tried to divide the enthalpies of transfer into single-ion values (in spite of limitations) similar to those made in the case of free energies of transfer of benzoic acid [7,22]. For reaction (1), we have

$$\Delta H_t^0(1) = \Delta H_t^0(H^+) + \Delta H_t^0(Bz^-) - \Delta H_t^0(HBz) \qquad (5)$$

or

$$\Delta H_t^0(H^+) + \Delta H_t^0(Bz^-) = \Delta H_t^0(1) + \Delta H_t^0(HBz) \qquad (6)$$

The thermodynamics of transfer for the ionization of benzoic acid $\Delta H_t^0(1)$ and neutral benzoic acid [23] (HBz) are recorded in Table 2. However, no value for $\Delta H_t^0(H^+)$ is available. Of the different methods of determination of single-ion enthalpies, the only useful method $\Delta H_t^0(ASPh_4^+) = \Delta H_t^0(BPh_4^-)$ also has its limitations [24]. The values of enthalpies of ion transfer are few and no value of $\Delta H_t^0(H^+)$ in alcohol + water mixtures is available. We, therefore, utilized the enthalpy values of the ‘isoelectric’ reaction

$$HPhen^+ \rightleftharpoons H^+ + Phen \qquad (7)$$

TABLE 2

Thermodynamics of transfer (in kJ $mol^{-1}$) of neutral HBz (1) and for the ionisation of benzoic acid (2) from water to ethanol–water mixtures at 298.1 K

| Wt% of alcohol | $\Delta G_t^0$ |  | $\Delta H_t^0$ |  | $-T\Delta S_t^0$ |  |
|---|---|---|---|---|---|---|
|  | (1) | (2) | (1) | (2) | (1) | (2) |
| 8.0 | −0.77 | 0.97 | 17.53 | −1.67 | −18.3 | 2.64 |
| 16.4 | −1.75 | 2.11 | 36.15 | −3.35 | −37.9 | 5.46 |
| 25.3 | −3.57 | 3.77 | 43.26 | 0.77 | −46.8 | 3.00 |
| 34.4 | −6.28 | 5.42 | 67.69 | −0.58 | −74.0 | 6.00 |
| 44.0 | −8.20 | 6.56 | 76.14 | 3.50 | −84.3 | 3.06 |
| 54.1 | −9.48 |  | 9.95 |  | −19.4 |  |

to calculate $\Delta H_t^0(H^+)$ in the way described earlier [25].

The $\Delta H_t^0(H^+)$ values have been recalculated. Thus, from the experimental values of $\Delta H_t^0(1)$. $\Delta H_t^0(HBz)$ and $\Delta H_t^0(H^+)$, $\Delta H_t^0(Bz^-)$ values have been calculated.

The values of thermodynamics of transfer from water to water + alcohol mixtures for $H^+$ and $Bz^-$ ions are recorded in Table 3.

We have also calculated the thermodynamics of benzoate ion in water using the $\Delta G^0(H^+)$ and $\Delta H^0(H^+)$ values from the literature [26] (after proper conversion into molar scale) and our own experimental values.

The results presented in Tables 2 and 3 indicate that the dominant contributions to the thermodynamics of transfer for the ionization process come from the $X^0(HBz)$ and $X^0(Bz^-)$ parts and they almost neutralize each other. The results also show that the contribution from $\Delta G_t^0$(neut) is more predominant than the electrostatic contributions $\Delta G_t^0$(el) arising from Born charging, and fully corroborate the idea

$$\Delta X_t^0(\text{ion}) = \Delta X_t^0(\text{neut}) + \Delta X_t^0(\text{el})$$

TABLE 3

Thermodynamics of transfer for $H^+$ and $Bz^-$ ions (in kJ $mol^{-1}$) from water to ethanol–water mixtures at 298.1 K

| Ethanol (wt%) | $\Delta G_t^0$ |  | $\Delta H_t^0$ |  | $T\Delta S_t^0$ |  |
|---|---|---|---|---|---|---|
|  | $H^+$ | $Bz^-$ | $H^+$ | $Bz^-$ | $H^+$ | $Bz^-$ |
| 8.0 | −1.08 | 1.21 | −0.83 | 16.69 | 0.25 | 15.48 |
| 16.4 | −1.83 | 2.07 | −1.71 | 34.51 | 0.12 | 32.44 |
| 25.3 | −2.70 | 2.83 | −1.40 | 45.43 | 1.30 | 42.60 |
| 34.4 | −3.38 | 1.83 | −0.88 | 67.99 | 2.50 | 66.16 |
| 44.0 | −4.52 | 3.05 | −1.03 | 80.67 | 3.49 | 77.62 |

$\Delta G_{H_2O}^0(H^+) = -1087.4$ kJ $mol^{-1}$, $\Delta H_{H_2O}^0(H^+) = -1083.2$ kJ $mol^{-1}$ and $\Delta S_{H_2O}^0(H^+) = -14$ J $K^{-1}$ $mol^{-1}$.

$\Delta G_{H_2O}^0(Bz^-) = 1115.8$ kJ $mol^{-1}$, $\Delta H_{H_2O}^0(Bz^-) = 1114.5$ kJ $mol^{-1}$ and $\Delta S_{H_2O}^0(Bz^-) = -4$ J $K^{-1}$ $mol^{-1}$.

The $\Delta G_t^0$(HBz) and $\Delta S_t^0$(HBz) (neutral HBz) have also been reported by Das et al. [27]. The increased stabilization of HBz$^-$ has been ascribed to dispersion interactions of the alkyl group of alcohol and HBz, coupled with hydrogen-bonding interactions. The peculiarities of $\Delta S_t^0$–composition profiles have been shown to result mainly from the effects of enhancement of water structure induced by the hydrocarbon moieties of alcohols and hydrogen-bonding effects. However, the results can be simply explained in terms of

(i) Rupture of bonds between solute molecules to remove the solute to the vapour phase ($\Delta H$ is +ve, $\Delta S$ is +ve. (ii) Creation of a cavity in the solvent which means rupture of H-bonds ($\Delta H$ is +ve, $\Delta S$ is +ve). (iii) Placement of the solute into the cavity. This step involves formation of a bond between solute and solvent ($\Delta H$ is −ve, $\Delta S$ is −ve).

The addition of benzoic acid means disruption of H-bonds between water and solute molecules and formation of new bonds leading to enthalpy and entropy increase. As the solubility increases with the addition of alcohol, greater disruption of H-bonds arises from more structured solvent mixtures leading to enthalpy and entropy increase. Beyond the structuration maximum of the solvent mixtures, two processes compete (i) Dissolution of greater amounts of HBz involving the formation of increased numbers of cavities. (ii) Formation of new solute–solvent bonds in the mixtures.

Initially, after the structuration maximum of alcohol–water mixtures, process (i) predominates over process (ii) leading to a gradual increase in enthalpy and entropy up to about 44 wt% ($X_2 = 0.2$–$0.3$) beyond which process (ii) predominates, leading to a decrease in enthalpy. Moreover, depolymerization leads to entropy increase but is accompanied by decrease in the total number of solvent molecules as well as increased solute–solvent bond formation. The introduction of Bz$^-$ involves disruption of H-bonds between solvent and solute molecules. Here Born charging ion–dipole and H-bonding forces predominate.

The enthalpy of transfer of Bz$^-$ is favourable from entropic considerations but unfavourable from enthalpic considerations. Both $\Delta H_t^0$(Bz$^-$) and $\Delta S_t^0$(Bz$^-$) increase continuously up to 44 wt%. However, $\Delta G_t^0$(Bz$^-$) is not favourable and passes through a maximum at 25 wt% of ethanol. $\Delta H_t^0$(H$^+$) is favourable, passing through a minimum at 16 wt% and decreasing again at 44 wt%, whereas $\Delta S_t^0$(H$^+$) passes through a minimum at 16 wt%.

Almost no reports exist for the determination of single-ion thermodynamics based on the dissociation of weak electrolytes. However, the single-ion values must be determined either by a method not involving any extrathermodynamic assumptions or we have to use different extrathermodynamic methods to get a reasonably consistent set of single-ion values to make meaningful correlations of results.

It is to be noted that the values given in Table 3 can be regarded as qualitative rather than quantitative as the uncertainty in the single-ion

($\Delta G^0$) values based on different extrathermodynamic assumptions is within 2 kcal mol$^{-1}$ [28]; even the closest values of $\Delta G^0(H^+)$ lie within 1 kJ mol$^{-1}$ [26]. The variation in $\Delta H^0(H^+)$ is more. Therefore, it is justifiable to assume an uncertainty not better than 1 kJ mol$^{-1}$ in the single-ion values in mixed solvents. Fluctuations in the single-ion values are thus to be expected.

The benzoic acid and benzoate ion are characterized by the presence of hydrophilic centres and hydrophobic centres leading to two different types of hydration. Thus both hydrophilic and hydrophobic interactions compete for water structure organization. The addition of benzoic acid or benzoate ion to water leads to the rupture of the tetrahedral structure of water. When two non-polar regions of benzoic acid or benzoate ion come close together, these regions would be shielded to a greater extent from interaction with water molecules. This would lead to the collapse of some of the quasi-crystalline water structure, resulting in gain in entropy. The addition of ethanol leads to the co-operative structure formation due to hydrophobic interactions and the maximum in the structure formation (entropy minimum) appears to be in the region of 50 wt%. For this particular system, the changes in thermodynamic properties can be attributed to specific solvation effects dependent on solvent mixtures and hydrophobic effects acting in opposite directions [29,30]. The specific effect appears to be greatest for $H^+$ ion and also to some extent for benzoate ion whereas the hydrophobic effect is greatest for $Bz^-$ and HBz and is maximal where maximum enhancement of the water structure occurs, i.e., about 44 wt% of ethanol.

It is to be noted that the addition of small quantities of ethanol causes a weakening of the hydrophobic interactions (HI). This effect is restricted to the region $0 \leqslant X(\mathrm{EtOH}) \leqslant 0.03$. At higher concentrations of alcohol, there is a pronounced increase in the strength of HI which persists up to $X(\mathrm{EtOH}) \approx 0.2$ beyond which HI becomes weak [31].

The thermodynamics of transfer of ions, however, can be explained assuming a two-stage mixture model, as suggested by Baumgartner and Atkinson [32] and used by Juillard [33].

The introduction of alcohol (having both hydrophilic and hydrophobic groups) will enhance the stabilization of the clusters corresponding to a gradual organization into fluctuating cages of water surrounding an alcohol molecule. These cages have a well-defined stoichiometry. The water structure is at first little affected (zone I) but becomes more and more organized until it attains maximum structuration corresponding to the stoichiometry of the cages of solid clathrate (zone II). Clathrate hydrate (EtOH, 17 $H_2O$; m.p. −72° C) [34–36] of type II presents two types of holes, large and small, able to encage molecules, and the structure is stabilized when the holes are occupied.

After a certain composition corresponding to a maximal formation of the cages, two phenomena, i.e., the apartition of the alcohol molecules and the condensation of cages occur, leading to the formation of merged clathrates (zone III).

It is well known that $H^+$ ion is strongly hydrated having a negative $-\Delta H_t^0(H^+)$. After maximum structuration, $H^+$ ions tend to attract water molecules leading to an enthalpy increase due to the disruption of ROH–$H_2O$ bonds.

The endothermic increase of enthalpy of anions is attributed to the enthalpy changes due to cavity formation, dispersion interactions, Born charging and ion–dipole interactions. In the structured region, anions are more easily accommodated in the interstitial locations (vacant holes) of the clathrate-like cages than in water. The endothermic $\Delta H_t^0(Bz^-)$ with increasing alcohol concentrations is due to (i) the weakness of the interactions between anions and free alcohol molecules, and (ii) development of interactions through dispersion forces between alcohol molecules and the benzoate ions which are highly solvated in organic media due to strong electron delocalization.

However, it is desirable to have more data on the thermodynamics of transfer before we can derive useful conclusions from such studies.

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