

## IONIZATION ENTHALPY OF BENZOIC ACID IN WATER–DIMETHYLSULFOXIDE MIXTURES

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### ABSTRACT

The ionization enthalpy of benzoic acid has been measured calorimetrically at 25°C in H<sub>2</sub>O–DMSO mixtures ranging from pure water to a maximum DMSO molar ratio  $X_{\text{DMSO}} = 0.80$ . With the increase of DMSO content, the ionization becomes more and more endothermic, and for  $X_{\text{DMSO}} = 0.8$  the ionization enthalpy is about 6 kcal mol<sup>-1</sup> higher than in water. By also measuring the solution enthalpy of crystalline benzoic acid in the mixtures, it has been shown that the solvation of the undissociated molecule is the main cause for the increase of the dissociation enthalpy. A comparison has been made between the relative enthalpies of benzoic and hydroxide ions in H<sub>2</sub>O–DMSO mixtures.

### INTRODUCTION

The ionic dissociation of water in water–dimethylsulfoxide (DMSO) mixtures and the related thermodynamic quantities have been the subject of our recent researches<sup>1,2</sup>. We found that the process is less endothermic in the mixtures than in pure water for a wide range of compositions ( $0.2 < X_{\text{DMSO}} < 0.65$ ). This is related to the improved solvation of the proton, which is enhanced by DMSO in the whole indicated composition range, and with the OH<sup>-</sup> solvation, which can still be solvated by water until the latter is not completely engaged in bonds with DMSO.

We found it rather interesting to study the behaviour of another weak electrolyte with a different anion, viz. benzoic acid. The size and the polarizability of the benzoate anion are quite different from those of OH<sup>-</sup>, and it is known from the literature<sup>3,4</sup> that even in the case of benzoic acid its dissociation decreases strongly, in H<sub>2</sub>O–DMSO mixtures, with the increase of the organic solvent content.

In this calorimetric research we measured not only the ionization enthalpy of benzoic acid (HBz) dissolved in various H<sub>2</sub>O–DMSO mixtures, but also the solution enthalpy of crystalline HBz in the mixtures, with the aim of determining whether the main cause of the dissociation enthalpy increase must be ascribed to a better solvation of the undissociated molecule or to a poor anion solvation.

## EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus has been described previously<sup>5,6</sup>. A reaction vessel with a capacity of 25 ml has been employed.

DMSO (Carlo Erba RP) has been purified according to Butler<sup>7</sup>. DMSO–water mixtures of known molar ratio have been prepared by weight, using purified DMSO and twice-distilled water. Those containing HCl have been prepared, always by weight, using purified DMSO and an aqueous HCl solution potentiometrically titrated, obtained by appropriate dilution of a standard 1.00 F HCl solution.

Sodium benzoate (NaBz) and benzoic acid (both Merck “pro analysis”) have been stored in a vacuum desiccator on P<sub>2</sub>O<sub>5</sub> and used as received.

The molar enthalpy of dissociation of HBz ( $\overline{\Delta H}_1$ ) in various H<sub>2</sub>O–DMSO mixtures of  $X$  molar ratio



has been obtained by the experimental measurement of

(a) the enthalpy of solution ( $\overline{\Delta H}_2$ ) of crystalline NaBz in the mixtures



(b) the enthalpy of solution ( $\overline{\Delta H}_3$ ) of the same salt in the same mixtures containing an excess of HCl



being  $\overline{\Delta H}_1 = \overline{\Delta H}_2 - \overline{\Delta H}_3$ .

The mixed solution and NaBz have been used in such amounts that the concentration of NaBz in various experiments was in the range  $3\text{--}5 \cdot 10^{-3}$  M. Therefore the  $\Delta H$  values that we measured can be considered at infinite dilution, taking into account also the fact that the highest DMSO molar ratio we used was  $X_{\text{DMSO}} = 0.8$ . This H<sub>2</sub>O–DMSO mixture has a dielectric constant value<sup>8,9</sup>  $\epsilon \cong 53$  at 25°C, and it is quite reasonable to suppose that the salt has completely dissociated. From the knowledge of the dissociation constants of water<sup>1,10,11</sup> and benzoic acid<sup>3,4</sup> in the H<sub>2</sub>O–DMSO mixtures it can also be inferred that the salt undergoes hydrolysis only in a very reduced percentage ( $\beta < 0.02\%$ ) and therefore the  $\Delta H$  experimentally measured in process (2) does not need to be corrected for concentration effect nor for hydrolysis. This has been experimentally checked by varying the NaBz concentration from  $3 \cdot 10^{-3}$  to  $1 \cdot 10^{-2}$  M; all the calculated  $\overline{\Delta H}_2$  values ranged within the experimental error limits. The HCl concentration in the mixed solutions used for process (3) was calculated to leave at the end of the process at least 50% excess of HCl, to assure the completeness of process (3).

The  $\overline{\Delta H}_1$  values, for each of the H<sub>2</sub>O–DMSO mixtures at  $X_{\text{DMSO}}$  molar ratio, are referred to the ionization process of *one mole of HBz, dissolved at infinite dilution in the mixed solvent with a molar ratio of  $X_{\text{DMSO}}$* , which gives one mole of protons and

one mole of  $\text{Bz}^-$  ions solvated in the same solvent. Therefore, on changing the solvent composition, it changes not only the standard state of the final products of the process (the two ions  $\text{H}^+$  and  $\text{Bz}^-$ ) but also the standard state of the initial product, i.e. the undissociated benzoic acid. For a better understanding of the meaning of the various  $\overline{\Delta H}_1$  values obtained in the different solvent mixtures, we also measured the solution enthalpy of crystalline benzoic acid ( $\overline{\Delta H}_4$ ) in the various solvent mixtures:



We used HBz concentrations of the order of  $0.5 \cdot 10^{-2}$  M and mixed solutions containing 10% excess of HCl to prevent the dissociation of dissolved HBz. We could get reliable results only for the solution experiments performed in mixed solutions with  $X_{\text{DMSO}} \geq 0.1$ , where the solution process is rather fast under the experimental conditions used. In pure water the phenomenon is very slow<sup>12</sup> and our apparatus cannot record the enthalpic effect accurately. For this reason we took from the literature<sup>13</sup> the enthalpy value of process (4) in pure water, assuming  $(\overline{\Delta H}_4)_w = 6.40 \text{ kcal mol}^{-1}$ .

All measurements were performed at  $t = 25 \pm 0.01^\circ\text{C}$ ; the average thermal jump into the cell during the experiments was about  $0.1^\circ\text{C}$ .

## RESULTS

In Table 1, the results obtained for  $\overline{\Delta H}_1$  in various DMSO–water solutions at the indicated DMSO molar ratios are reported.

TABLE 1

MOLAR IONIZATION ( $\overline{\Delta H}_1$ ) AND SOLUTION ( $\overline{\Delta H}_4$ ) ENTHALPY OF BENZOIC ACID IN DMSO– $\text{H}_2\text{O}$  SOLUTIONS OF VARIOUS MOLAR RATIO AT  $25^\circ\text{C}$

$X_{\text{DMSO}}$	$\overline{\Delta H}_1$ (kcal mol <sup>-1</sup> )	$\overline{\Delta H}_4$ (kcal mol <sup>-1</sup> )	$\Delta H_0$ ( $\overline{\Delta H}_1 + \overline{\Delta H}_4$ )
0	$0.10 \pm 0.01$	$6.40 \pm 0.1^a$	$6.50 \pm 0.1$
0.1	$0.48 \pm 0.02$	$4.17 \pm 0.05$	$4.65 \pm 0.05$
0.2	$1.21 \pm 0.01$	$4.82 \pm 0.07$	$6.03 \pm 0.07$
0.3	$1.88 \pm 0.02$	$4.12 \pm 0.01$	$6.00 \pm 0.02$
0.4	$2.43 \pm 0.01$	$4.03 \pm 0.04$	$6.46 \pm 0.04$
0.5	$3.38 \pm 0.04$	$2.64 \pm 0.04$	$6.02 \pm 0.06$
0.6	$3.30 \pm 0.08$	$2.05 \pm 0.06$	$5.35 \pm 0.10$
0.7	$4.29 \pm 0.08$	$1.64 \pm 0.09$	$5.93 \pm 0.12$
0.8	$6.07 \pm 0.09$	$1.46 \pm 0.03$	$7.53 \pm 0.09$

<sup>a</sup> From ref. 13.

Each result is the difference between the average values obtained from at least four experiments related to process (2) and four experiments related to process (3); average deviations are indicated next to the tabulated values.

The values of  $\overline{\Delta H}_4$ , the solution enthalpy of crystalline HBz in the various mixtures, and those of  $\overline{\Delta H}^\circ = \overline{\Delta H}_1 + \overline{\Delta H}_4$ , related to the process



are also reported in Table 1. In process (5), when changing the solvent composition, *only the thermodynamic status of the final products is changed.*

Our experimental value for  $(\overline{\Delta H}_1)_{\text{w}}$  is in very good agreement with the literature data<sup>14,15</sup>.

The enthalpies reported in Table 1 are better expressed as the differences between the values measured in the mixed solvent of  $X_{\text{DMSO}}$  molar ratio and that obtained in pure water, so that  $\delta\overline{\Delta H} = (\overline{\Delta H})_{\text{x}} - (\overline{\Delta H})_{\text{w}}$ . The values of  $\delta\overline{\Delta H}_1$ ,  $\delta\overline{\Delta H}_4$  and  $\delta\overline{\Delta H}^\circ$  obtained from the data of Table 1 are plotted vs.  $X_{\text{DMSO}}$  in Fig. 1. We notice that, with regard to the values of  $\delta\overline{\Delta H}_4$  and  $\delta\overline{\Delta H}^\circ$ , the reliability of such values is mainly dependent on the accuracy related to the literature value<sup>13</sup> for  $(\overline{\Delta H}_4)_{\text{w}}$ .

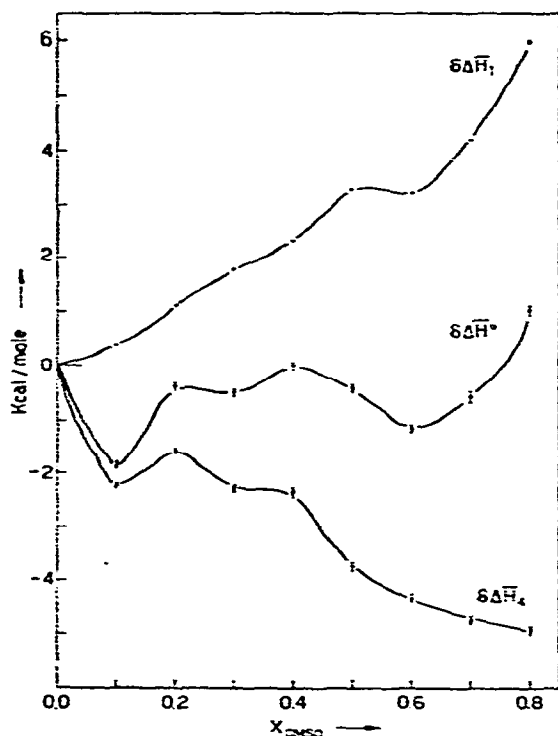


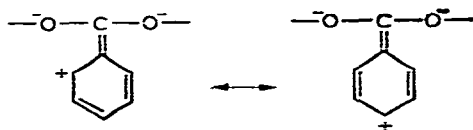
Fig. 1. Transfer enthalpies for the benzoic acid solution and ionization in DMSO-H<sub>2</sub>O mixtures at  $t = 25^\circ\text{C}$  (see text).

## DISCUSSION

The  $\delta\overline{\Delta H}_1$  curve of Fig. 1 shows clearly that, *if the undissociated HBz dissolved in the solution is taken as initial reference state*, the ionization enthalpy undergoes a

rather fast rise with the increase of the DMSO content, and for  $X_{\text{DMSO}} \cong 0.8$  the process becomes about  $6 \text{ kcal mol}^{-1}$  more endothermic than in pure water. The free energy of ionization, which can be calculated from the literature  $\text{p}K$  data<sup>3,4</sup>, follows the same trend, becoming about  $4 \text{ kcal mol}^{-1}$  more than in pure water for  $X_{\text{DMSO}} = 0.5$  and about  $7 \text{ kcal mol}^{-1}$  for  $X_{\text{DMSO}} = 0.8$ . Therefore the behaviour of HBz is quite different from that of water<sup>1,2</sup> in the sense that the entropy factor is not so very important for the ionic dissociation which is hindered as the organic solvent content increases, and the acid dissociates less and less mainly for enthalpic reasons.

The increase of  $\overline{\Delta H}_1$  when going from water to  $\text{H}_2\text{O}$ -DMSO mixtures is obviously related to a progressive increase of the solvation of the undissociated molecule and to a concurrent desolvation of the  $\text{Bz}^-$  anion, as it is usually noticed when the solvation properties of  $\text{H}_2\text{O}$ -DMSO mixtures toward neutral molecules and anions are considered. Particularly with regard to HBz, the solvation of the neutral molecule by the DMSO content can be enhanced for dipolar resonance structure as<sup>16</sup>:



whereas similar forms for the  $\text{Bz}^-$  anion, as



are unlikely because two negative charges are thus brought close together.

Our calorimetric measurements of the solution enthalpy of the crystalline HBz lead to the conclusion that, at least from the enthalpic point of view, the increase of solvation of the undissociated HBz plays a much more important role than the desolvation of the ionic products. The  $\delta\overline{\Delta H}_4$  values (Fig. 1) are in fact always negative, and the solution of the acid in a  $\text{H}_2\text{O}$ -DMSO mixture of  $X_{\text{DMSO}} = 0.8$  is about  $5 \text{ kcal mol}^{-1}$  more exothermic than in pure water.

The increase of the dissociation enthalpy of HBz with the DMSO content of the solvent mixture is therefore mainly dependent on the stabilization of the initial state (the undissociated acid molecule) rather than on the desolvation of the final ionic products. Even from this point of view the behaviour of HBz is different from that<sup>2</sup> of  $\text{H}_2\text{O}$ .

The  $\delta\overline{\Delta H}^\circ$  values reported in Fig. 1 represent the transfer enthalpy of the two ions  $\text{H}^+$  and  $\text{Bz}^-$  from pure water to  $\text{H}_2\text{O}$ -DMSO mixtures. It can be noticed that, all together, the solvation of the two ions is slightly better in the mixtures than in pure water until  $X_{\text{DMSO}} = 0.75$ ; only beyond this concentration value is  $\delta\overline{\Delta H}^\circ$  positive.

This indicates a partial compensation between the improved proton solvation and the progressive benzoate anion desolvation with the increase of the organic solvent content. The two effects cannot be separated without invoking some extrathermodynamic assumption; a comparison is nevertheless possible between the enthalpy of the two anions  $\text{Bz}^-$  and  $\text{OH}^-$  in the various solvent mixtures by using the transfer enthalpy values for the couple  $\text{H}^+ \text{OH}^-$  which we recently measured<sup>1</sup>. For each  $\text{H}_2\text{O}$ -DMSO mixture, the difference between the transfer enthalpy of the couple  $\text{H}^+ \text{Bz}^-$  and that of the couple  $\text{H}^+ \text{OH}^-$  represents the difference of enthalpy between the solvated benzoate anion  $(\text{Bz}^-)_x$  and the solvated hydroxide ion  $(\text{OH}^-)_x$  less the difference (which is constant) between the enthalpies of these two ions in pure water. By setting this last difference arbitrarily equal to zero, the values of  $\overline{\Delta H}_{\text{Bz}^- - \text{OH}^-} = \delta \overline{\Delta H}_{\text{HBz}}^\circ - \delta \overline{\Delta H}_{\text{H}_2\text{O}}^\circ$  are plotted in Fig. 2 versus the solvent composition.

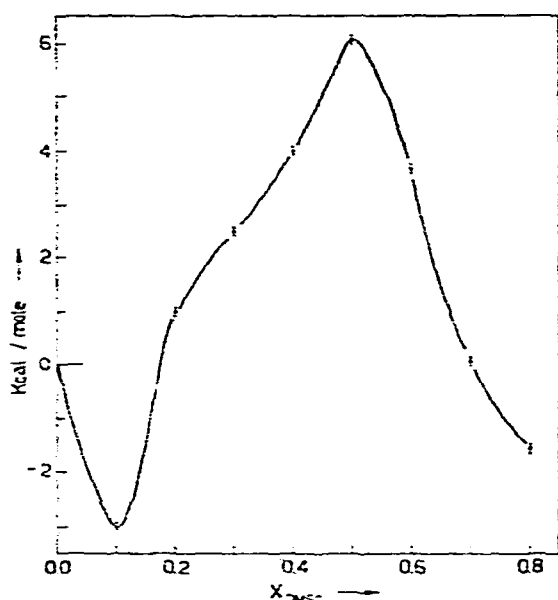


Fig. 2.  $\overline{H}_{\text{Bz}^-} - \overline{H}_{\text{OH}^-}$  in various  $\text{H}_2\text{O}$ -DMSO mixtures. The  $\Delta H_{\text{Bz}^- - \text{OH}^-}$  in pure water has been arbitrarily put as zero.

It is interesting to notice, from the trend of the curve in Fig. 2, that in the mixtures with a low DMSO content ( $X_{\text{DMSO}} = 0.1$ ) in which the structure of water is promoted, the  $\text{Bz}^-$  ion is stabilized more than  $\text{OH}^-$ . With the increase of the DMSO content, the amount of free water molecules decreases and as a result the benzoate ion becomes more desolvated than the hydroxide ion. This trend lasts until  $X_{\text{DMSO}} = 0.5$ , where the destabilization of  $\text{Bz}^-$  relative to  $\text{OH}^-$  shows a sharp maximum. With a further increase of the DMSO content,  $\overline{\Delta H}_{\text{Bz}^- - \text{OH}^-}$  quickly decreases, thus indicating that the solvation of the two anions becomes more similar. It is in fact probable that even the hydroxide ion, in the DMSO-rich mixtures, undergoes a drastic reduction of its solvation<sup>17</sup>.

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