

THE EFFECT OF MEDIUM ON THE DISSOCIATION OF THE *meta*-CARBOXY ANILINE ION. A TAUTOMERIC EFFECT

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ABSTRACT

A thermodynamic study of the dissociation of the *m*-carboxy aniline ion in water–DMSO mixtures, ranging from pure water up to 0.8 DMSO mole fraction is presented

A tautomeric zwitterion equilibrium seems to influence the ionization trend in water-rich solutions

INTRODUCTION

The thermodynamic study of the dissociation of *meta*-, *para*- and *ortho*-hydroxy aniline ions in water–dimethylsulfoxide (DMSO) mixtures has formed the subject of a study in our laboratory [1–3]. The *meta*-hydroxy aniline ion is the weakest base in the whole mole fraction range [3]. Indeed, *meta*-hydroxy aniline displays the strongest solvation mostly in DMSO-rich solutions. This could mean that the large dipole of DMSO stabilizes the benzene charge of *m*-hydroxy aniline by virtue of the favourable interaction between the NH₂ and OH groups. Electrophilic attack of the proton on the benzene ring is likely to occur.

In the present work, the behaviour of the *meta*-carboxy aniline ion in the same mixtures has been examined. In particular, it seemed interesting to compare both the effects displayed by the OH group (σ acceptor and π donor) and the COOH group (σ and π acceptor) on NH₂.

The different behaviours of OH and COOH substituents in the *meta* position can be ascribed to the stabilizing and destabilizing interaction with the amino group, respectively.

meta-Carboxy aniline also displays, in water-rich solutions, a tautomeric zwitterion equilibrium [4] which could influence the ionization trend.

EXPERIMENTAL PROCEDURE

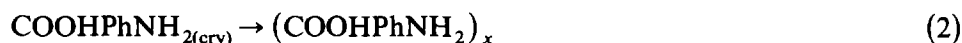
The calorimetric apparatus has been previously described [5,6]. DMSO (Carlo ErbaRPrade) was purified according to the procedure of Synnot and

Butler [7]. DMSO–water mixtures were prepared, by weight, from purified DMSO- and CO₂-free, twice-distilled water. The mole fraction of DMSO in these mixtures ranged from 0.0 to 0.8. An aqueous solution of 0.99 M HCl was prepared from a standard solution; its concentration was checked by potentiometric titration. *m*-Carboxy aniline was recrystallized from water–alcohol mixtures; its m.p. was checked before use. The compound was handled in a dry-box filled with dry nitrogen. The weighing of the compound was also performed in the dry-box.

The ionization process of the *m*-carboxy aniline ion (COOHPhNH₃⁺) in the various water–DMSO mixtures of *x* mole fraction can be represented as

$$(\text{COOHPhNH}_3^+)_x \rightarrow (\text{H}^+)_x + (\text{COOHPhNH}_2)_x \quad (1)$$

The molar enthalpy of ionization, $\Delta\bar{H}_1$, of COOHPhNH₃⁺ was obtained [5,6] by measuring the molar enthalpy of solution, $\Delta\bar{H}_2$, of crystalline *m*-carboxy aniline in the mixed solvent of *x* mole fraction



and the molar enthalpy of neutralization, $\Delta\bar{H}_3$, of the same compound in the same mixture containing an excess of HCl



The molar enthalpy, $\Delta\bar{H}_1$, of process (1) can be obtained [5,6] by subtracting the two values $\Delta\bar{H}_2$ and $\Delta\bar{H}_3$.

In processes (2) and (3), concentrations ranging from $2 \times 10^{-3}m$ to $4 \times 10^{-3}m$ were used. Therefore, the $\Delta\bar{H}_1$ values can be considered at infinite dilution [5,6].

For each water–DMSO mixture at x_{DMSO} mole fraction, these values refer to the ionization process of one mole of COOHPhNH₃⁺, dissolved at infinite dilution in 1000 g of the mixed solvents, yielding one mole of COOHPhNH₂ molecules and one mole of protons solvated in the same amount of solvent. In the literature [4], the $\text{p}K_a/1$ values of process (1) at 20°C are reported. In water-rich solutions the $\text{p}K_a/1$ values are related to the dissociation from COOHPhNH₃⁺ to the tautomeric zwitterion equilibrium $\text{COO}^- \text{PhNH}_3^+ \rightleftharpoons \text{COOHPhNH}_2$ while in DMSO-rich solutions only the COOHPhNH₂ form is present.

From these data and from the ΔH_1^0 values reported in Table 1, the $\text{p}K_a/1$ values at 25°C were calculated [1,2]. From the $\text{p}K_a/1$ values at 25°C, the free energy, ΔG_1^0 , relative to process (1) and the $T\Delta S^0$ values were calculated using the Gibbs–Helmholtz equation.

In the mole fraction range 0.0–0.1 the apparent $\text{p}K_a/1$ and ΔG^0 values are calculated.

The initial standard state to which ΔG^0 values of ionization refer is defined as an ideal 1 *m* solution of COOHPhNH₃⁺ behaving as an infinitely dilute solution.

RESULTS

Table 1 shows the ΔG_1^0 , ΔH_1^0 and $T\Delta S_1^0$ values for process (1) obtained for the *m*-carboxy aniline ion. Table 2 shows the enthalpy values of processes (2) and (3).

For the sake of comparison, it is convenient to express the ionization enthalpy values, ΔH_1^0 , of the carboxy substituent anion as the difference between the values obtained in the mixed solvent at mole fraction x and in pure water so that

$$\delta\Delta H^0 = (\Delta H_1^0)_x - (\Delta H_1^0)_{x=0}$$

In a similar way, the values of $\delta\Delta G_1^0$ and $T\delta\Delta S_1^0$ can be defined and calculated. These three values are relative to the transfer of the ionization

TABLE 1

Free energy, enthalpy and entropy values for the ionization of *m*-carboxyaniline ion in DMSO-water solutions of various mole fractions at 25°C^a

x_{DMSO}	ΔG_1^0	ΔH_1^0	$T\Delta S_1^0$
0.0	4.16	1.60	-2.56
0.1	3.96	2.80	-1.16
0.2	3.56	2.40	-1.16
0.3	3.22	1.64	-1.58
0.4	3.08	1.08	-2.00
0.5	3.00	1.01	-1.97
0.6	3.04	1.26	-1.78
0.7	3.14	1.97	-1.17
0.8	3.28	2.23	-1.05

^a All thermodynamic quantities given in kcal mole⁻¹

TABLE 2

Enthalpy values of processes (2) and (3) for the *m*-carboxy aniline ion in DMSO-water solutions of various mole fractions at 25°C

x_{DMSO}	ΔH_2^0	ΔH_3^0
0.0	5.13	3.53
0.1	8.04	5.24
0.2	8.08	5.68
0.3	6.48	4.84
0.4	4.59	3.51
0.5	3.22	2.21
0.6	2.20	0.94
0.7	1.77	-0.20
0.8	1.29	-0.94

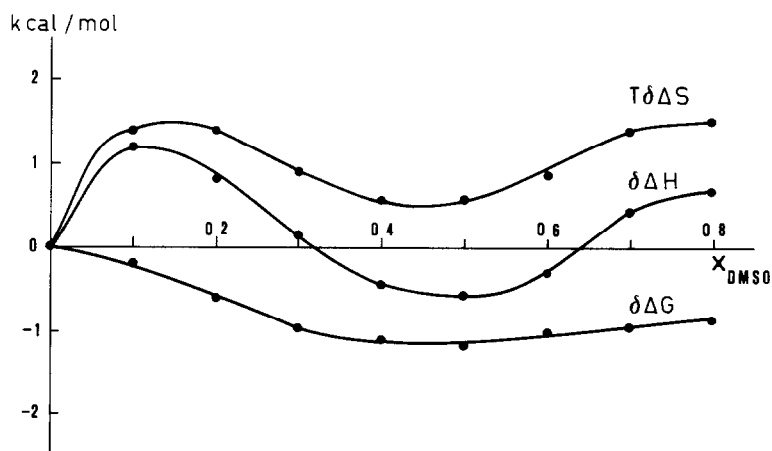


Fig 1 Thermodynamic quantities for the transfer of the ionization of the *m*-carboxy aniline ion from pure water to DMSO-water mixtures as a function of the mole fraction

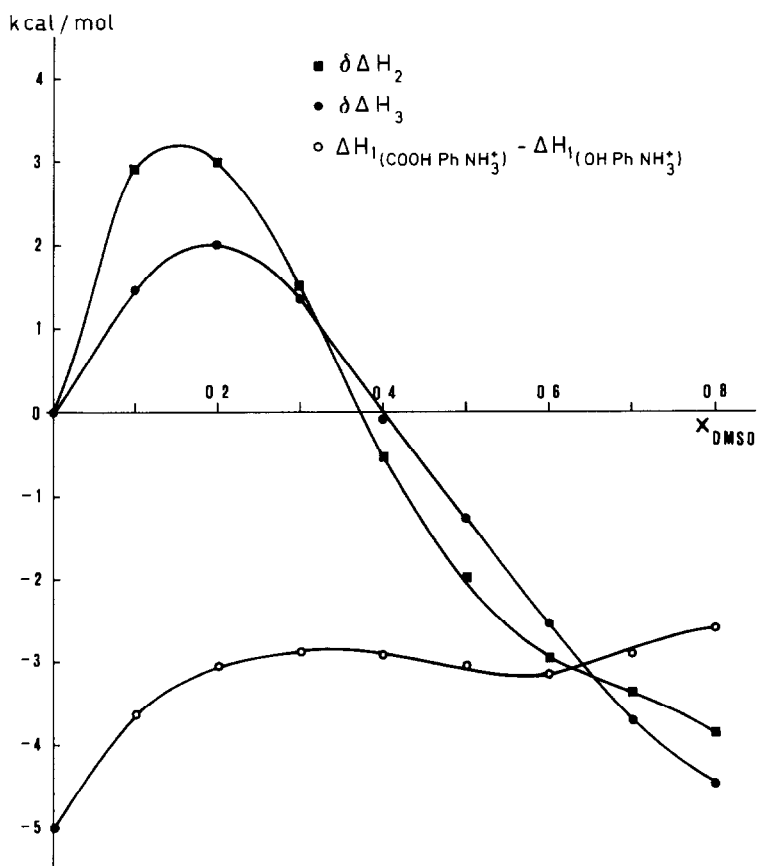


Fig 2 Transfer enthalpies of *m*-carboxy aniline and *m*-carboxy aniline ion from pure water to DMSO-water mixtures as a function of the mole fraction Difference in the enthalpy deprotonation of *meta*-carboxy and *meta*-hydroxy aniline ions as a function of the mole fraction

process, while the $\delta\Delta H_2^0$ and $\delta\Delta H_3^0$ values represent the transfer enthalpy of substituted aniline and the substituted aniline ion, respectively, from pure water to mixed solvent. All these data are plotted against x_{DMSO} in Figs. 1 and 2.

DISCUSSION

From Fig. 1 it can be inferred that the $\delta\Delta H_1^0$ term is favourable to process (1) for $0.3 \leq x_{\text{DMSO}} \leq 0.6$ while outside this range the dissociation of the carboxy aniline ion is hindered, mostly in water-rich solutions.

The $\delta\Delta G_1^0$ and $T\delta\Delta S_1^0$ terms are always favourable to dissociation. None of these terms can be identified with the driving force of process (1).

The enthalpy trend can be explained taking into account the solvation enthalpies of the carboxy-aniline and carboxy aniline ion. Fig. 2 shows that the aniline ion is more solvated than the aniline molecule in the whole fraction range with the exception of $0.3 \leq x_{\text{DMSO}} \leq 0.6$.

By comparing the *meta*-carboxy and *meta*-hydroxy anilines by means of the difference in the enthalpy deprotonation $(\Delta H_1^0)_{\text{COOH Ph NH}_2^+} - (\Delta H_1^0)_{\text{OH Ph NH}_2^+}$ (Fig. 2), it can be inferred that the *meta*-carboxy derivative is a weaker effective base than the *meta*-hydroxy derivative in the whole mole fraction range. This clearly has to be related to the greater electron-withdrawing inductive effect displayed by the carboxyl group. It is also noteworthy that in pure water there is a maximum in the difference in the

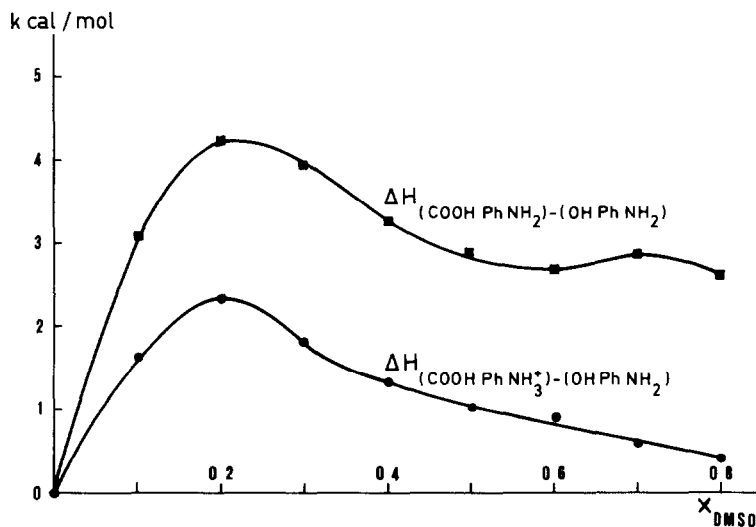


Fig. 3 Differences in the solvation enthalpies between the ion couples and the undissociated molecule couples of *meta*-carboxy and *meta*-hydroxy compounds in various DMSO-water mixtures

enthalpy deprotonation. This difference sharply increases as far as $x_{\text{DMSO}} = 0.2$. Beyond this mole fraction the difference becomes constant. Indeed, for the carboxy compound the zwitterion form is predominant in pure water (60%) [4] and also greatly solvated by water molecules, while in DMSO-rich solutions only the undissociated molecule is present, so that the difference in deprotonation enthalpy can be ascribed mostly to the different inductive effect of COOH and OH groups.

This behaviour is confirmed in Fig. 2 which shows how the solvation of the undissociated molecule sharply decreases in $0.0 \leq x_{\text{DMSO}} \leq 0.2$ where the zwitterion and the water molecules quickly decrease. Beyond this mole fraction the zwitterion form disappears and the undissociated neutral molecule is solvated by DMSO molecules.

Finally, the differences in solvation enthalpy between the ions $\Delta H_{(\text{COOHPhNH}_2^+)-(\text{OHPhNH}_2^+)}^0$ and the undissociated molecules $\Delta H_{(\text{COOHPhNH}_2)-(\text{OHPhNH}_2)}^0$ of *meta*-carboxy and *meta*-hydroxy compounds were calculated as previously shown [5,6] and plotted in Fig. 3.

Figure 3 shows that in the whole mole fraction range the order of the transfer is $\text{OHPhNH}_2 > \text{COOHPhNH}_2$. This supports the conclusion, according to the Perturbation Molecular Orbital Theory [8], that for the carboxy derivative the interaction between the first group NH_2 and the second group COOH is dominated by the σ electron-withdrawing effect of the latter, which destabilizes the benzene ring. To the contrary, for *meta*-hydroxy aniline, the π donor effect of the OH group stabilizes the benzene ring.

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