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THERMODYNAMICS OF IONIZATION PROCESSES FOR CHLORO-SUBSTITUTED BENZOIC ACIDS IN WATER–DIMETHYLSULFOXIDE MIXTURES AT 25°C

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ABSTRACT

The ionization enthalpies of *o*-, *m*-, and *p*-chloro-benzoic acid were measured calorimetrically at 25°C in water–DMSO mixtures ranging from pure water up to 0.8 DMSO mole fraction. In the same mole fraction range, molar free energies and entropies were calculated for the ionization processes.

The different results obtained for the three acids were explained by taking into account the different effects displayed on the solvation and ionization phenomena by the chlorine atom in the various positions on the aromatic ring.

Using the transfer enthalpy of benzoic acid in the same mixtures as a reference point, a solvation sequence is proposed both for the ions and the undissociated molecules.

INTRODUCTION

The ionic dissociation of benzoic acid (HBzO) in water–dimethylsulfoxide (DMSO) mixtures and the related thermodynamic quantities have been the subject of a recent paper of ours[1]. We could observe an increase in the dissociation enthalpy of HBzO when the DMSO content of the solvent mixture was increased. We ascribed this behaviour to the stabilization of the initial state (the undissociated acid molecule) rather than to the desolvation of the final ionic products.

We thought it interesting to study the behaviour of *o*-, *m*-, and *p*-chlorobenzoic acids in the same mixtures, in order to elucidate the different effect of the chlorine atom in the various positions on the solvation and ionization phenomena.

EXPERIMENTAL AND PROCEDURE

The calorimetric measurements were performed by means of:

(a) an LKB 8721-1 reaction and solution calorimeter, and an LKB 8725-1 100 ml reaction vessel;

(b) an LKB 8721-2 titration calorimeter, a Metrohm multi-Dosimat E 415 10 ml motor burette connected to a Dosifix E 442 programmer, and an LKB 8726-1 100 ml titration vessel;

(c) an LKB 7603 thermostatic bath and an LKB 7602 A-3 proportional controller (10–40°C).

The measurement and calibration circuits described in previous papers[2,3] were modified as follows: a Hewlett-Packard 6133A constant voltage supply was used for the resistance bridge, instead of the nickel–cadmium battery set; a Hewlett-Packard 5325-B universal counter in place of the Jaquet 309 DR electric watch; a Leeds & Northrup Speedomax W recorder instead of the Keithley 370 strip chart recorder.

DMSO (Carlo Erba, RP grade) was purified according to Butlers procedure[4]. DMSO–water mixtures were prepared by weight, from purified DMSO and CO_2-free twice-distilled water. The mole fraction of these mixtures ranged from 0.1 to 0.8. Aqueous solutions of 0.98 N HCl and 0.10 N NaOH were prepared from standard solutions; their concentrations were checked by potentiometric titrations. *o*-, *m*- and *p*-chlorobenzoic acids (K & K) were stored in a vacuum dissicator on P_2O_5, and underwent no further purification. The $NaBzO_s$ solutions (where subscript s indicates the substituted acids) were prepared by adding an amount of NaOH solution, containing approximately one equivalent of alkali, to the *o*-, *m*- and *p*-chlorobenzoic acid dissolved in the mixed solvent. As a result of this addition, 100 g of the DMSO–water solution at a known mole fraction X′ were obtained. The concentrations of the sodium salts were always in the range from $2 \cdot 10^{-3}$ to $4 \cdot 10^{-3}$ F. An amount of acid, about 4 or 5% of the original content, was not converted to salt and remained as free acid, to avoid the presence of free alkali. The dissociation process of $HBzO_s$ in the various water–DMSO mixtures of X mole fraction can be represented as

$$(HBzO_s)_X \rightarrow (H^+)_X + (BzO_s^-)_X \tag{1}$$

The molar enthalpy of dissociation of $HBzO_s$ ($\overline{\Delta H_1}$) has been obtained by the experimental measurement of:

The molar enthalpy of reaction ($\overline{\Delta H_2}$) of the sodium salt $NaBzO_s$, dissolved in the mixed solvent of X′ mole fraction, with 0.98 N HCl:

$$(BzO_s^-)_{X'} + (Na^+)_{X'} + (H^+)_{aq} + (Cl^-)_{aq} \rightarrow (HBzO_s)_X + (Na^+)_X + (Cl^-)_X \tag{2}$$

The molar enthalpy of dilution of the same amount of 0.98 N HCl in the same solvent mixture at X′ mole fraction:

$$(H^+) +_{aq} (Cl^-)_{aq} \rightarrow (H^+)_X + (Cl^-)_X \tag{3}$$

In processes (2) and (3), the symbols X′ and X refer to the DMSO mole fraction in the solvent mixture, respectively, before and after the process.

From the dissociation constant values of water[6] and the substituted chlorobenzoic acids[7], it can also be inferred that the salts undergo very little hydrolysis ($\beta < 0.02\%$). Therefore, it is not necessary to correct the $\overline{\Delta H_2}$ values experimentally measured in process (2) for hydrolysis.

The hypothetical process represented as

$$(HBzO_s)_X + (Na^+)_X \rightarrow (BzO^-)_{X'} + (Na^+)_{X'} + (H^+)_X \tag{4}$$

has a thermal effect $\overline{\Delta H_4}=\overline{\Delta H_3}-\overline{\Delta H_2}$. The molar enthalpy $\overline{\Delta H_1}$ of process (1) should be obtained by adding the $\overline{\Delta H_4}$ values to the molar transfer enthalpy of $NaBzO_s$ (at infinite dilution) from solvent X′ to solvent X. The transfer process can be described as

$$(BzO_s^-)_{X'}+(Na^+)_{X'} \rightarrow (BzO_s^-)_X+(Na^+)_X \tag{5}$$

process (1) being the sum of processes (4) and (5). It has to be remarked, incidentally, that the difference (X′−X) turns out to be very small for each couple: in the most unfavourable case it was $2\cdot10^{-4}$, when the DMSO final mole fraction was 0.8.

The transfer enthalpy of Na^+ and BzO_s^- ions should not be very different from that of Na^+ and BzO^-; for the latter ions an average variation of 0.88 kcal mol^{-1} could be observed[1] when the mole fraction of the solvent mixture was varied with 0.1.

We think that the error introduced by neglecting the thermal effect of process (5) under our experimental conditions falls within the precision limits of our measurements, which are at best 0.6%. Therefore, we take the $\overline{\Delta H_4}$ of reaction (4) as the molar enthalpy of dissociation ($\overline{\Delta H_1}$) of substituted chlorobenzoic acids dissolved in DMSO–water solutions at 25 °C.

For each of the water–DMSO mixtures at X_{DMSO} mole fraction, these $\overline{\Delta H_1}$ values refer to the ionization process of one mole of $HBzO_s$, dissolved at infinite dilution in the mixed solvent, yielding one mole of protons and one mole of BzO_s^- ions solvated in the same solvent. Therefore, if the solvent composition is changed, there is a variation in the standard state not only for the final products (H^+ and BzO_s^- ions) but also for the initial substance (the undissociated acid).

In order to refer process (1) to one initial standard state only, we measured the solution enthalpy of the crystalline chlorobenzoic acids ($\overline{\Delta H_6}$) in water–DMSO mixtures at various mole fractions:

$$HBzO_{s_{cr}} \rightarrow (HBzO_s)_X \tag{6}$$

therefore the process

$$HBzO_{s_{cr}} \rightarrow (H^+)_X+(BzO_s^-)_X \tag{7}$$

is the sum of processes (6) and (1). In process (7), only the final products vary their thermodynamic state upon variation of the solvent composition.

In processes (6) and (4), concentrations ranging from $2\cdot10^{-3}$ to $4\cdot10^{-3}$ F were used. Therefore, the measured $\overline{\Delta H_1}$ and $\overline{\Delta H_6}$ values can be considered at infinite dilution[7]. As regards *p*-chlorobenzoic acid, we could obtain reliable results only when the solution heat experiments were performed in mixed solvents with $X_{DMSO}\geq0.4$, where the solution process is rather fast under the experimental conditions used. At lower mole fractions, the dissolution is very slow and our apparatus could not record the enthalpic effect accurately.

The enthalpy value, at $X_{DMSO}=0$, of process (6) for the *o*-chlorobenzoic acid was not measured, but found in the literature[8].

All the measurements were carried out at 25±0.01 °C, the average thermal jump in the cell during the experiments being about 0.1 °C.

RESULTS

Tables 1, 2 and 3 show the $\overline{\Delta H}$ values of processes (1), (6), and (7), obtained with the three chlorobenzoic acids in DMSO–water solutions, as functions of the DMSO mole fraction.

TABLE 1

MOLAR ENTHALPY OF IONIZATION ($\overline{\Delta H}_1$) AND SOLUTION ($\overline{\Delta H}_6$) FOR *o*-CHLOROBENZOIC ACID IN DMSO–WATER SOLUTIONS OF VARIOUS MOLE FRACTIONS AT 25°C

X_{DMSO}	$\overline{\Delta H}_1$ (kcal mol^{-1})	$\overline{\Delta H}_6$ (kcal mol^{-1})	$\overline{\Delta H}_7$ ($\overline{\Delta H}_1+\overline{\Delta H}_6$)
0	−2.5 ± 0.01	6.43	3.93
0.1	−1.26 ± 0.02	5.97 ± 0.02	4.71 ± 0.03
0.2	2.95 ± 0.02	5.57 ± 0.02	8.52 ± 0.04
0.3	2.81 ± 0.03	5.97 ± 0.02	8.78 ± 0.04
0.4	3.12 ± 0.01	3.84 ± 0.02	6.96 ± 0.02
0.5	4.17 ± 0.04	3.25 ± 0.01	7.42 ± 0.04
0.6	7.73 ± 0.04	2.70 ± 0.03	10.45 ± 0.08
0.7	12.72 ± 0.08	2.02 ± 0.02	14.74 ± 0.08
0.8	11.95 ± 0.09	1.86 ± 0.02	13.81 ± 0.09

TABLE 2

MOLAR ENTHALPY OF IONIZATION ($\overline{\Delta H}_1$) AND SOLUTION ($\overline{\Delta H}_6$) FOR *m*-CHLOROBENZOIC ACID IN DMSO–WATER SOLUTIONS OF VARIOUS MOLE FRACTIONS AT 25°C

X_{DMSO}	$\overline{\Delta H}_1$ (kcal mol^{-1})	$\overline{\Delta H}_6$ (kcal mol^{-1})	$\overline{\Delta H}_7$ ($\overline{\Delta H}_1+\overline{\Delta H}_6$)
0	0.030 ± 0.009	6.50 ± 0.01	6.53 ± 0.01
0.1	0.260 ± 0.01	6.60 ± 0.07	6.86 ± 0.07
0.2	2.17 ± 0.03	6.70 ± 0.04	8.87 ± 0.05
0.3	3.75 ± 0.05	5.72 ± 0.04	9.47 ± 0.06
0.4	2.46 ± 0.01	5.61 ± 0.03	8.07 ± 0.03
0.5	5.56 ± 0.04	4.08 ± 0.01	9.64 ± 0.04
0.6	6.96 ± 0.06	3.72 ± 0.02	10.68 ± 0.06
0.7	7.13 ± 0.09	3.42 ± 0.01	10.55 ± 0.09
0.8	11.89 ± 0.07	2.77 ± 0.01	14.66 ± 0.07

TABLE 3

MOLAR ENTHALPY OF IONIZATION ($\overline{\Delta H}_1$) AND SOLUTION ($\overline{\Delta H}_6$) FOR *p*-CHLOROBENZOIC ACID IN DMSO–WATER SOLUTIONS OF VARIOUS MOLE FRACTIONS AT 25°C

X_{DMSO}	$\overline{\Delta H}_1$ (*kcal mol*$^{-1}$)	$\overline{\Delta H}_6$ (*kcal mol*$^{-1}$)	$\overline{\Delta H}_7$ ($\overline{\Delta H}_1+\overline{\Delta H}_6$)
0	0.25 ± 0.01	—	—
0.1	0.41 ± 0.02	—	—
0.2	2.03 ± 0.03	—	—
0.3	4.99 ± 0.01	—	—
0.4	5.27 ± 0.02	3.84 ± 0.07	9.11 ± 0.07
0.5	3.18 ± 0.05	3.97 ± 0.04	7.15 ± 0.06
0.6	4.20 ± 0.05	3.85 ± 0.04	8.05 ± 0.06
0.7	7.24 ± 0.07	3.38 ± 0.01	10.62 ± 0.07
0.8	11.66 ± 0.09	3.21 ± 0.01	14.87 ± 0.09

Each figure reported for process (1) is the difference between an average of at least four values relative to process (2) and a similar average for process (3); the standard deviations are indicated next to the tabulated values.

In the literature[5], the $pK_{a/1}$ values of process (1) at 20°C are reported for *o*-, *m*- and *p*-chlorobenzoic acid. From these data and from the $\overline{\Delta H}_1$ values reported in Tables 1, 2 and 3, we calculated the $pK_{a/1}$ values at 25°C, using the well-known equation

$$pK_{25°C} = pK_{20°C} - \frac{\overline{\Delta H}_1 \Delta T}{1.987\, T_1 T_2\, 2.303}$$

From $pK_{a/1}$ at 25°C, we calculated the free energy $\overline{\Delta G}_1$ relative to process (1), and the $T\overline{\Delta S}_1$, values through the Gibbs-Helmholtz equation.

For comparison, it is convenient to express the ionization enthalpy $\overline{\Delta H}_1$ of the chloro-substituted acids as a difference between the values obtained in the mixed solvent of X mole fraction and in pure water so that:

$$\delta\overline{\Delta H}_1 = (\overline{\Delta H}_1)_X - (\overline{\Delta H}_1)_{X=0}$$

In a similar way, the values of $\delta\overline{\Delta G}_1$ and $T\delta\overline{\Delta S}_1$ can be defined and calculated. These three δ-values are relative to the transfer-of-ionization process, while $\delta\overline{\Delta H}_6$ and $\delta\overline{\Delta H}_7$ represent the transfer enthalpy of the undissociated molecule and of the two ions H^+ and BzO_x^-, respectively, from pure water to the mixed solvent. All these thermodynamic data are plotted against X_{DMSO} in Figs. 1, 2 and 3.

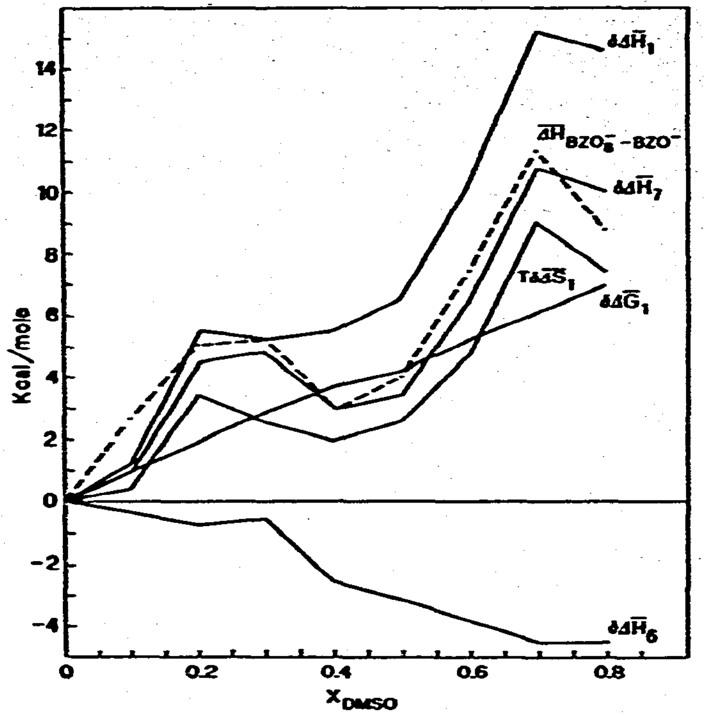


Fig. 1. Thermodynamic quantities for the transfer of *o*-chlorobenzoic acid from water to DMSO–water mixtures, as a function of the mole fraction at 25 °C.

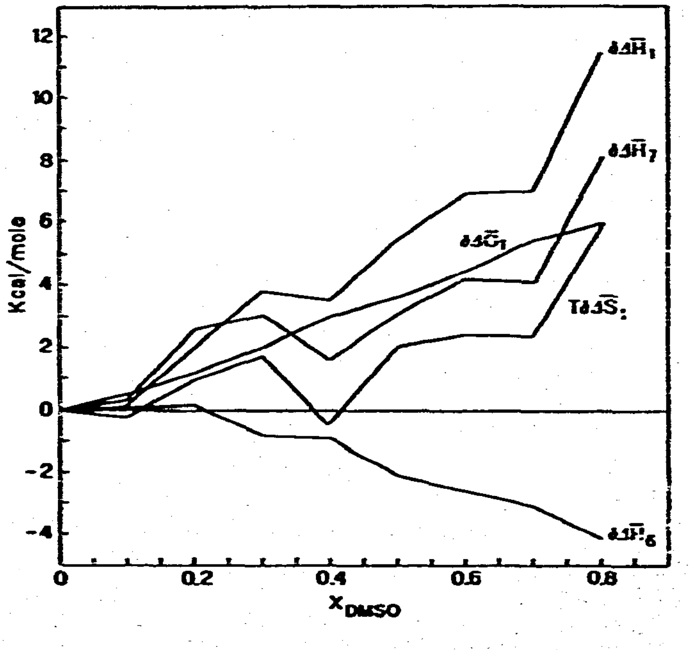


Fig. 2. Thermodynamic quantities for the transfer of the *m*-chlorobenzoic acid from water to DMSO–water mixtures, as a function of the mole fraction at 25 °C

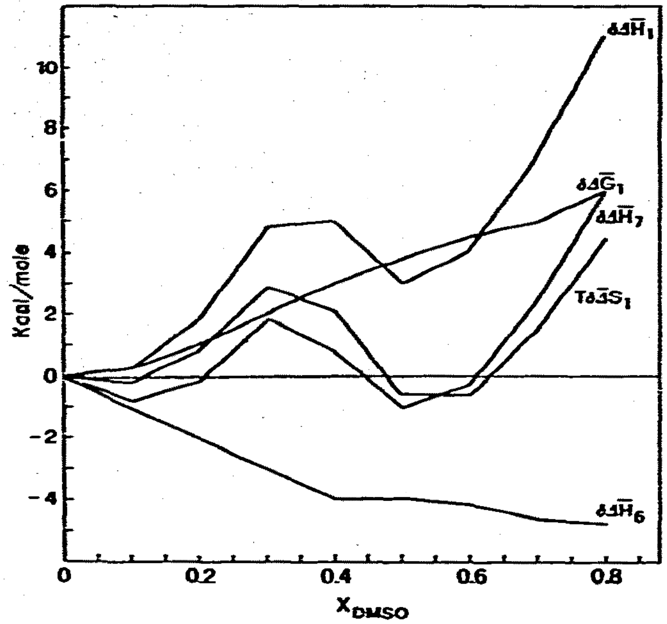


Fig. 3. Thermodynamic quantities for the transfer of the *p*-chlorobenzoic acid from water to DMSO–water mixtures, as a function of the mole fraction at 25°C.

DISCUSSION

As regards the *o*-chlorobenzoic acid (Fig. 1), the increase in the $\overline{\Delta H}_1$ values observed when water is progressively substituted with DMSO can be related to a better solvation of the undissociated molecule paralleled by a desolvation of the ionic products, according to the equation

$$\delta\overline{\Delta H}_1 = \delta\overline{\Delta H}_7 - \delta\overline{\Delta H}_6$$

From the curves of Fig. 1, it can be also inferred that, from the enthalpic point of view, the desolvation of the BzO_s^- anion plays a much more important role than the solvation of the undissociated molecule $HBzO_S$ (H^+ ions are always better solvated in water–DMSO mixtures than in pure water)[9–11]; with respect to this point, $HBzO_s$ and HBzO display an opposite behaviour.

It may be interesting to compare the solvation enthalpy of the two anions BzO_s^- and BzO^- in the various solvent mixtures, by making use of the transfer enthalpy values of the couple H^+–BzO^-, which we recently measured[1]. For each water–DMSO mixture, the difference in the solvation enthalpy between the solvated chlorobenzoic anion $(BzO_s^-)_X$ and the solvated benzoic anion $(BzO^-)_X$ was calculated as

$$\overline{\Delta H}_{BzO_s^-/BzO^-} = \delta\overline{\Delta H}_{7\,(HBzO_s)} - \delta\overline{\Delta H}_{7\,(HBzO)}$$

and the left-hand side values are plotted in Fig. 1 (dotted line) as a function of the solvent composition. It can be noticed that the chloro-substituted anion is even more desolvated than the unsubstituted one, at least in the X_{DMSO} range from 0 to 0.8. Therefore, the introduction of a chlorine atom in the *ortho* position decreases the solvation of the benzoic anion. This fact can be almost exclusively ascribed to the induction effect of chlorine, which takes part of the negative charge away from the $-COO^-$ group, thus decreasing the interactions between water and the anion (hydrogen bond, dipole–dipole attraction, etc.)[12,13].

TABLE 4

RELATIVE ACIDITY VALUES OF BENZOIC AND *o*-CHLOROBENZOIC ACIDS IN DMSO–WATER SOLUTIONS OF VARIOUS MOLE FRACTIONS AT 25°C

X_{DMSO}	$pK_{benzoic\ acid} - pK_{o-benzoic\ acid}$
0	1.26
0.1	1.04
0.2	0.85
0.3	0.85
0.4	0.93
0.5	1.18
0.6	1.02
0.7	1.16
0.8	1.16

The maximum shown by the $\overline{\Delta H}_{BzO_s^-/BzO^-}$ curve at a X_{DMSO} value between 0.2 and 0.3 can be related to a drastic desolvation of the *o*-chlorobenzoic anion, which is affected much more than BzO^- by a variation in the H_2O/DMSO molar ratio from 9:1 ($X_{DMSO} = 0.1$) to 2.3:1 ($X_{DMSO} = 0.3$). All these results are in agreement with the relative acidity values of benzoic acid and its *o*-chlorosubstituted derivative, expressed as the difference of the p*K* values of the two substances and reported as a function of X_{DMSO} (Table 4). These relative acidity data were obtained from the literature[5] and a previous work of ours[6]. As can be seen, there is a minimum at the same 0.2–0.3 mole fraction value.

When $X_{DMSO} > 0.5$, the molar ratio H_2O/DMSO is lower than 1, and consequently the unsubstituted anion BzO^- is better solvated than BzO_s^-. When X_{DMSO} is allowed to vary from 0.3 to 0.5, the difference in the solvation enthalpy between the solvated substituted anion $(BzO_s^-)_X$ and the unsubstituted one $(BzO^-)_X$ decreases, owing to a better solvation of $(BzO_s^-)_X$ and a worse solvation of $(BzO^-)_X$, with respect to what could be observed at $X_{DMSO} < 0.3$.

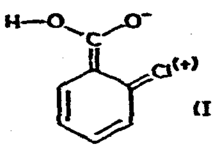
The values of $\delta\overline{\Delta G}_1$ show that the acid dissociation is always hindered by an increase of DMSO in the solvent mixture, while the term $T\delta\overline{\Delta S}_1$ turns out to be always favourable to the process. $\delta\overline{\Delta H}_1$ values are always larger than the corresponding $\delta\overline{\Delta G}_1$ and $T\delta\overline{\Delta S}_1$ values. Thus, the enthalpic term can be identified with the driving force of the process.

Clearly, the ionization of *o*-chlorobenzoic acid produces more disorder than HBzO[15].

As regards *m*-chlorobenzoic acid, the ionization process has a trend similar to the *o*-chloro derivative. The increase observed in the $\overline{\Delta H}_i$ curve when the DMSO content is increased depends much more on the anion desolvation than the undissociated molecule solvation.

A comparison of the curves of the transfer enthalpy for the ions ($\delta\overline{\Delta H}_7$) and for the undissociated molecules ($\delta\overline{\Delta H}_6$) of the *ortho* and *meta* acids suggest that the *m*-chlorobenzoic anion is solvated to a larger extent, in the various mixtures, than the *o*-chloro anion. On the other hand, the undissociated *o*-chloro molecule is solvated to a greater degree than the *m*-chloro acid. The chlorine atom in a *meta* position attracts the negative charge of the carboxylate anion more weakly than in the *ortho* position, thus allowing stronger interactions between the $-COO^-$ group and the water molecules.

The better solvation of the *o*-chlorobenzoic acid undissociated molecule, with respect to *meta*, can be explained by admitting that the *ortho* form can be in resonance with the dipolar structure (I), while no similar structure exists for the *meta* acid owing to structure (I)



(I)

stronger dipole–dipole interactions are allowed with the solvent molecules (see Figs. 1 and 2), mostly in DMSO-rich mixtures.

As previously stated, reliable results with *p*-chlorobenzoic acid could be obtained only when $X_{DMSO} \geq 0.4$.

TABLE 5

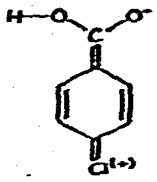
MOLAR ENTHALPY OF SOLUTION ($\overline{\Delta H}_s$; kcal mol^{-1}) FOR SOME SUBSTITUTED BENZOIC ACIDS IN WATER AT 25°C

	NO_2	Cl	OH
ortho	5.35	5.43	6.35
meta	5.59	6.50[a]	6.17
para	8.90	—	7.72

[a] Experimental value by us.

On the grounds of the similar R^+ and I^- effects[14] displayed by the OH^- and Cl^- substituents, and taking account of the solution enthalpy values ($\overline{\Delta H}_s$) of the substituted benzoic acids[8] shown in Table 5, it seemed reasonable to assume a $\overline{\Delta H}_s$ value of about 8±0.5 kcal mol^{-1} for *p*-chlorobenzoic acid in water.

Figure 3 shows clearly that, if a linear trend for $\delta\overline{\Delta H}_6$ is assumed between pure water and $X_{DMSO}=0.4$, the transfer enthalpy of the undissociated molecules plays a very important role in the dissociation of *p*-chlorobenzoic acid. Actually, on account of the fact that for X_{DMSO} values ranging from 0.4 to 0.8 the $\overline{\Delta H}_s$ values of this substance are practically constant, it can be inferred that it is highly probable that a dramatic increase in the solvation of the *p*-chlorobenzoic acid undissociated molecules takes place within the range between pure water and $X_{DMSO}=0.4$. The constancy of $\overline{\Delta H}_s$ from 0.4 to 0.8 mole fraction can be related to a dipolar structure (II) that can be thought to be in resonance with the uncharged structure in the *p*-chlorobenzoic acid molecule. In this structure (II) a true dipole is present; this can interact effectively with the molecules of the mixture, and, therefore, the acid molecule is completely solvated already at low DMSO mole fractions.



(II)

In comparison with the *ortho* and *meta* isomers, the negative charge on the *p*-chlorobenzoic anion is more tightly localized on the $-COO^-$ group, owing to the weaker electron-attractive effect of the chlorine atom. Therefore, the transfer of the *p*-chlorobenzoic anion from pure water to DMSO mixtures is easier than *o*- and *m*-chloro isomers (Fig. 3); the transfer tendency decreases according to the sequence $BzO^- > p\text{-}BzO_s^- > m\text{-}BzO_s^- > o\text{-}BzO_s^-$, as can be deduced from the transfer enthalpy values. On the contrary, for the transfer of the undissociated molecules, the following order is observed:

$$HBzO \cong p\text{-}HBzO_s > o\text{-}HBzO_s > m\text{-}HBzO_s$$

The $T\delta\Delta S_1$ term is favourable to the *p*-chlorobenzoic acid dissociation throughout the whole mole fraction range, except for the intervals from 0 to 0.1 and from 0.5 to 0.6, where process (1) is anti-entropic and order-forming in comparison with the same process taking place in pure water.

From the ionization processes of the three acids, the typical features[15,16] of the water/DMSO mixtures are confirmed. The greatest difficulty in organizing the solvent molecules around the ions is experienced at about $X_{DMSO}=0.5$. In fact, a minimum in the $T\delta\widetilde{\Delta S}_1$ function has been detected at $X_{DMSO}=0.4$ for the *o*- and *m*-acids, and at 0.5–0.6 for the *p*-isomer. Furthermore, the ions solvating power of the mixture shows a maximum at about $X_{DMSO}=0.5$. We think that the latter property could be explained by considering that when this mole fraction is attained, an equal number of water and DMSO molecules can be found in the solvent mixture, and this could possibly represent the best condition in order to solvate both cations and anions.

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