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

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ABSTRACT

The ionization and solution enthalpies of nitrobenzoic isomers were measured calorimetrically at 25°C in water–DMSO mixtures ranging from pure water up to 0.8 mole fraction DMSO.

In the same solutions, the ΔG^0 values for the ionization process have been determined by potentiometric measurements.

The anomalous trend of the enthalpy of solvation of the *ortho* anion was explained taking into account the variation of the resonance effect as a function of the solvent composition.

INTRODUCTION

The ionization of chlorobenzoic acids and nitrophenol isomers in water–dimethylsulfoxide mixtures have formed the subject of extended research in our laboratory[1, 2].

In the present work, the behaviour of the nitrobenzoic acids in the same mixtures has been examined. In particular, it seemed interesting to compare both the effects displayed by the chlorine atom $(I^- R^+)$ and the nitrogroup $(I^- R^-)$ on –COOH.

The difference in behaviour between Cl and $-NO_2$ can be related to the resonance, the greater size and the different inductive effects of the nitrogroup.

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus has been described previously[1, 2]. DMSO (Carlo Erba, RP grade) was purified according to the procedure[3] of Synnot and Butler. DMSO–water mixtures were prepared by weight from purified DMSO and CO_2-free twice-distilled water. The mole fraction of DMSO in these mixtures ranged from 0.1 to 0.8. Aqueous solutions of 0.99 M HCl and 0.098 M NaOH were prepared from standard solutions; their concentrations were checked by potentiometric titrations. The *o-*, *m-* and *p*-nitrobenzoic acids (all K and K products) were purified by crystalliza-

tion from water–alcohol mixtures; their m.p.'s were checked before use. The $NaBzO_s$ solutions (where the subscript indicates the substituted acids) were prepared by adding a NaOH solution of known molarity to the o-, m- and p-nitrobenzoic acids dissolved in the mixed solvent. As a result of this addition, 100 g of the DMSO–water solution at X' mole fraction were obtained.

The ionization process of $HBzO_s$ in the various water–DMSO mixtures of X mole fraction can be represented as

$$(HBzO_s)_X \rightarrow (H^+)_X + BzO_s^-)_X \qquad (1)$$
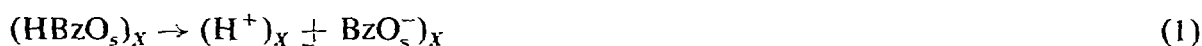
The molar enthalpy $\Delta\bar{H}_1$ of ionization of $HBzO_s$ was obtained[1, 2] by experimental measurement of:

The molar enthalpy of reaction ($\Delta\bar{H}_2$) of $NaBzO_s$, dissolved in the mixed solvent of X' mole fraction, with 0.99 M HCl

$$(BzO_s^-)_{X'} + (Na^+)_{X'} + (H)_{aq} + Cl^-)_{aq} \rightarrow (HBzO_s)_X + (Na^+)_X + (Cl^-)_X \qquad (2)$$
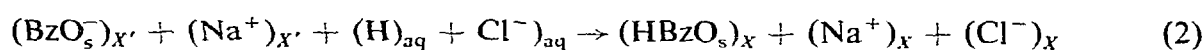
The molar enthalpy of solution $\Delta\bar{H}_3$ of the same amount of 0.99 M HCl, in the same solvent mixture at X' mole fraction

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

The molar enthalpy $\Delta\bar{H}_1$ of process (1) can be obtained[1, 2] by subtracting the two values $\Delta\bar{H}_3$ and $\Delta\bar{H}_2$ and by adding to this difference the $\Delta\bar{H}_4$ values related to the molar transfer enthalpy of $NaBzO_s$ (at infinite dilution) from solvent X' to solvent X.

$$(BzO^-)_{X'} + (Na^+)_{X'} \rightarrow (BzO^-)_X + (Na^+)_X \qquad (4)$$
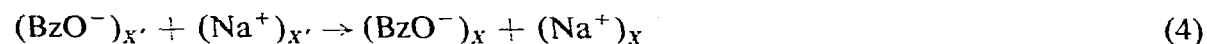
For a better understanding of the $\Delta\bar{H}_1$ values obtained in the different solvent mixtures, the solution enthalpies of the crystalline substituted benzoic acids in the various solvent mixtures were measured.

$$HBzO_{s(cr)} \rightarrow (HBzO_s)_X \qquad (5)$$

so that the $\Delta\bar{H}_6 = \Delta\bar{H}_5 + \Delta\bar{H}_1$ values obtained for the process

$$HBzO_{s(cr)} \rightarrow (H^+)_X + (BzO_s^-)_X \qquad (6)$$

refer to an identical initial state.

As regards p-nitrobenzoic acid, it is impossible to obtain reliable results in the mixtures with $X_{DMSO} < 0.4$, because the dissolution rate is very slow and the calorimetric apparatus cannot record the enthalpic effect.

Potential measurements were made with an Orion 801 digital pH meter; the glass electrode was an Orion 91-01-00. The details of calorimetric and potentiometric measurements have been described previously[1, 2, 4, 5].

RESULTS

Tables 1–3 show the $\Delta\bar{H}$ values of processes (1), (5) and (6) obtained for the three nitrobenzoic acids.

TABLE 1

MOLAR ENTHALPY OF IONIZATION ($\Delta \bar{H}_1$) AND SOLUTION ($\Delta \bar{H}_5$) FOR o-NITROBENZOIC ACID IN DMSO–WATER SOLUTIONS OF VARIOUS MOLE FRACTIONS AT 25°C

X_{DMSO}	$\Delta \bar{H}_1$ (kcal mole^{-1})	$\Delta \bar{H}_5$ (kcal mole^{-1})	$\Delta \bar{H}_6$ ($\Delta \bar{H}_1 + \Delta \bar{H}_5$)
0	-0.781 ± 0.01	5.30 ± 0.03	4.52 ± 0.03
0.1	0.24 ± 0.01	7.15 ± 0.03	7.39 ± 0.03
0.2	0.87 ± 0.02	6.43 ± 0.03	7.30 ± 0.04
0.3	4.04 ± 0.04	5.55 ± 0.11	9.59 ± 0.11
0.4	5.48 ± 0.05	3.80 ± 0.04	9.28 ± 0.06
0.5	10.49 ± 0.04	2.66 ± 0.00	13.15 ± 0.04
0.6	7.57 ± 0.04	2.09 ± 0.03	9.66 ± 0.05
0.7	7.52 ± 0.04	1.70 ± 0.05	9.22 ± 0.06
0.8	9.49 ± 0.05	1.41 ± 0.01	10.90 ± 0.05

TABLE 2

MOLAR ENTHALPY OF IONIZATION ($\Delta \bar{H}_1$) AND SOLUTION ($\Delta \bar{H}_5$) FOR m-NITROBENZOIC ACID IN DMSO–WATER SOLUTIONS OF VARIOUS MOLE FRACTIONS AT 25°C

X_{DMSO}	$\Delta \bar{H}_1$ (kcal mole^{-1})	$\Delta \bar{H}_5$ (kcal mole^{-1})	$\Delta \bar{H}_6$ ($\Delta \bar{H}_1 + \Delta \bar{H}_5$)
0	0.44 ± 0.01	5.60 ± 0.04	6.04 ± 0.04
0.1	2.10 ± 0.01	6.40 ± 0.06	8.50 ± 0.06
0.2	6.67 ± 0.05	7.53 ± 0.02	14.20 ± 0.05
0.3	10.43 ± 0.08	6.44 ± 0.03	16.87 ± 0.08
0.4	14.61 ± 0.08	4.32 ± 0.02	18.93 ± 0.08
0.5	16.12 ± 0.13	3.27 ± 0.07	19.39 ± 0.13
0.6	16.53 ± 0.10	2.67 ± 0.00	19.20 ± 0.10
0.7	11.94 ± 0.11	2.07 ± 0.09	14.01 ± 0.11
0.8	12.50 ± 0.12	1.85 ± 0.01	14.35 ± 0.11

TABLE 3

MOLAR ENTHALPY OF IONIZATION ($\Delta \bar{H}_1$) AND SOLUTION ($\Delta \bar{H}_5$) FOR p-NITROBENZOIC ACID IN DMSO–WATER SOLUTIONS OF VARIOUS MOLE FRACTIONS AT 25°C

X_{DMSO}	$\Delta \bar{H}_1$ (kcal mole^{-1})	$\Delta \bar{H}_5$ (kcal mole^{-1})	$\Delta \bar{H}_6$ ($\Delta \bar{H}_1 + \Delta \bar{H}_5$)
0	0.43 ± 0.01	8.8	9.23
0.1	0.65 ± 0.02		
0.2	1.50 ± 0.03		
0.3	6.76 ± 0.01		
0.4	7.15 ± 0.02	3.54 ± 0.01	10.69 ± 0.02
0.5	6.58 ± 0.05	3.42 ± 0.16	10.00 ± 0.16
0.6	7.94 ± 0.05	2.72 ± 0.04	10.66 ± 0.06
0.7	10.18 ± 0.07	2.91 ± 0.01	13.09 ± 0.07
0.8	15.90 ± 0.09	2.71 ± 0.00	18.61 ± 0.09

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

The pK_a values obtained from potentiometric measurements, were used to calculate the $\Delta\bar{G}$ values at different temperatures. These values may be related to T, according to Ives and Pryor[6], by the equation

$$\Delta\bar{G} = a + bT + cT^2$$

where the coefficients a, b and c were obtained by the least-squares method. $T\,\Delta\bar{S}^0$ values were calculated using the Gibbs–Helmholtz equation.

For comparison, it is convenient to express the ionization enthalpy as the difference between the values obtained in the mixed solvent of X mole fraction and in pure water so that

$$\delta\Delta\bar{H} = (\Delta\bar{H}_1)_X - (\Delta\bar{H})_{1X=0}$$

In a similar way, the values of $\delta\Delta\bar{G}_1$ and $T\delta\Delta\bar{S}_1$ can be defined and calculated.

The three values are relative to the ionization transfer process, while the $\delta\Delta\bar{H}_5$ and $\delta\Delta\bar{H}_6$ values represent the transfer enthalpy of the undissociated molecules and of the two ions H^+ and BzO_5^-, respectively, from pure water to the mixed solvent. All these data are plotted against X_{DMSO} in Figs. 1–3.
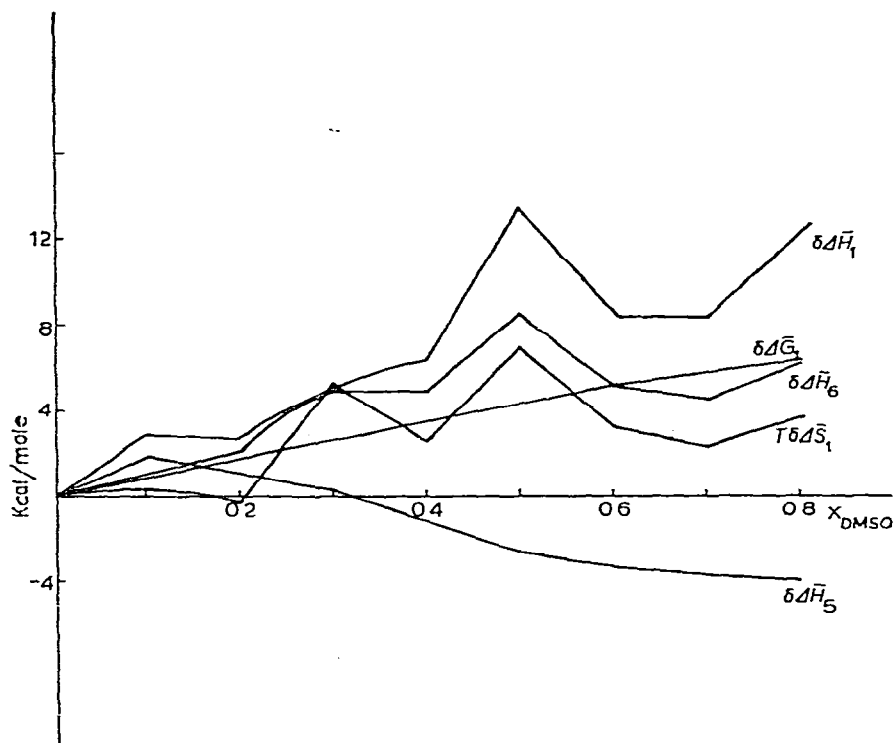

Fig. 1. Thermodynamic quantities for the transfer of the o-nitrobenzoic acid from pure water to DMSO–water mixtures, as function of the mole fraction at 25 °C.
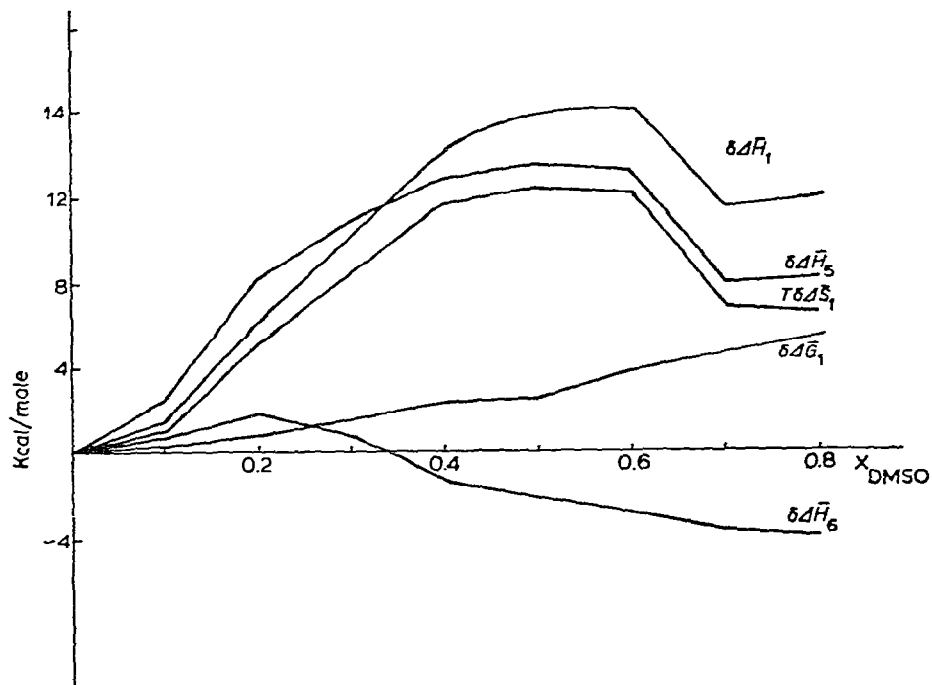
Fig. 2. Thermodynamic quantities for the transfer of the *m*-nitrobenzoic acid from pure water to DMSO–water mixtures, as function of the mole fraction at 25 °C.
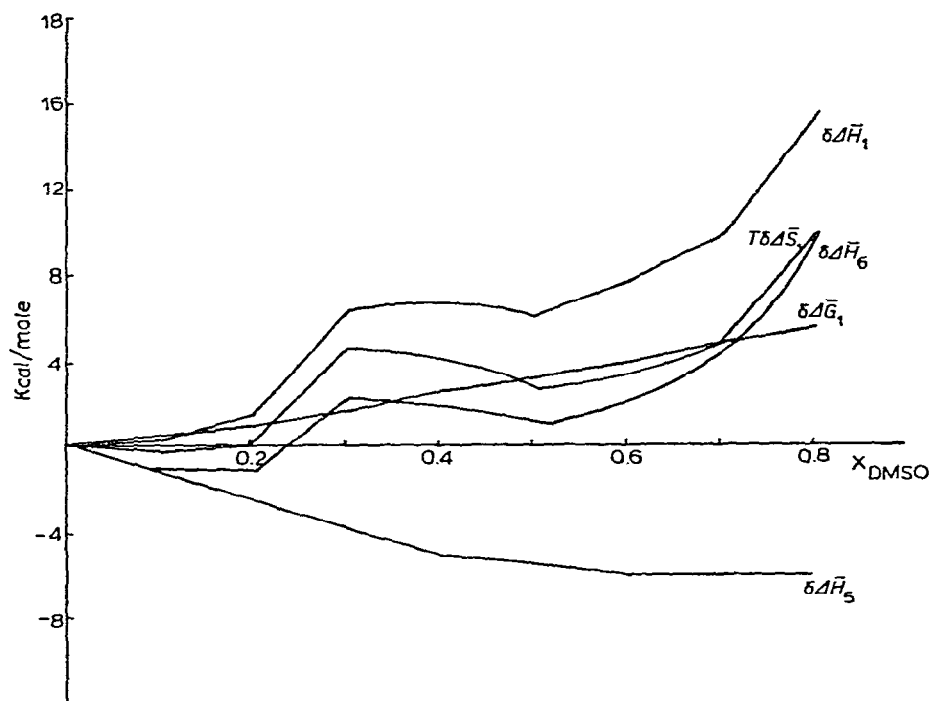

Fig. 3. Thermodynamic quantities for the transfer of the *p*-nitrobenzoic acid from pure water to DMSO–water mixtures, as function of the mole fraction at 25 °C.
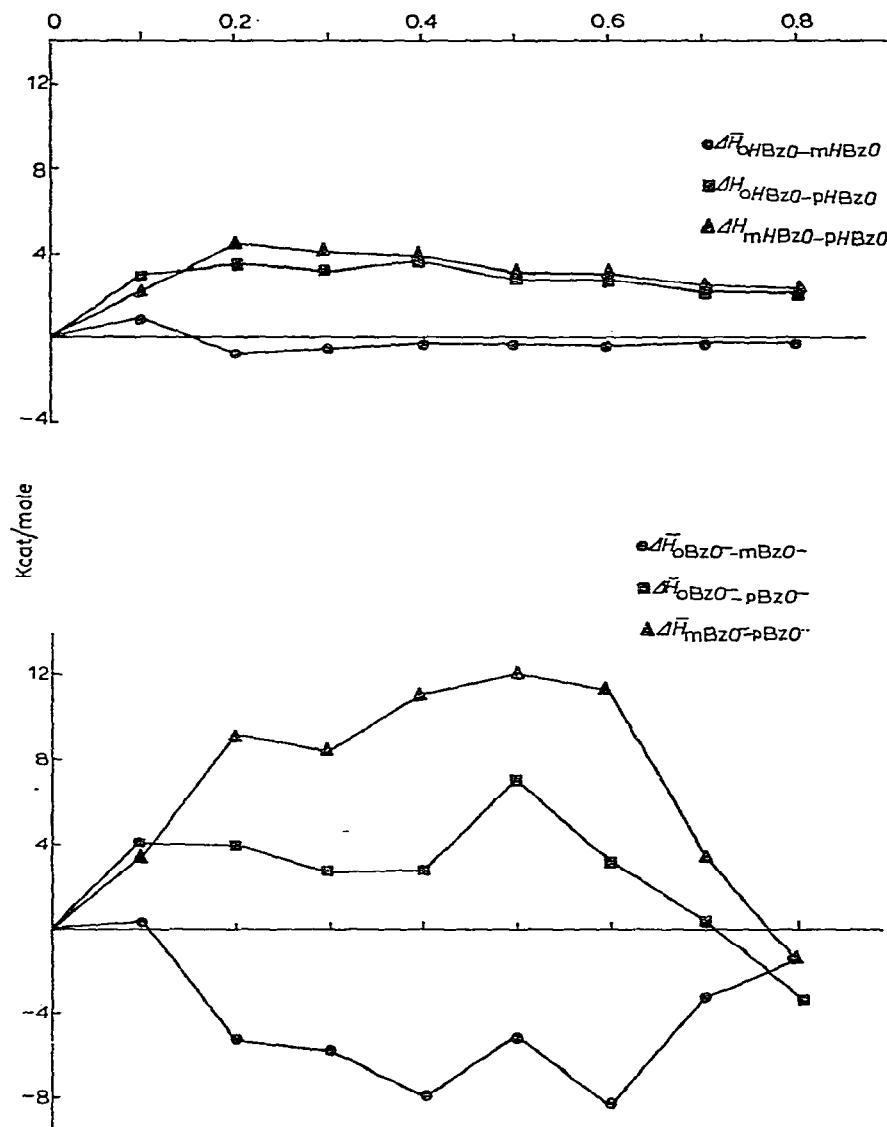
Fig. 4. Differences in the solvation enthalpy between (a) the nitro anion couples and (b) between the undissociated nitro-molecule couples, in various DMSO–water mixtures. The differences in the hydration enthalpy both between the anion couples and between the undissociated molecule couples are arbitrarily set equal to zero.

DISCUSSION

A comparison of Figs. 1–3 suggests that m-nitrobenzoic acid, from the enthalpic point of view, undergoes ionization with greater difficulty than o- and p-nitrobenzoic acids.

This fact can be ascribed to the different solvation which the molecules and the ions of the three nitro isomers undergo in the mixtures.

The difference in solvation enthalpy between the *ortho* and *meta* solvated nitro anions, was calculated as[2]

$$\Delta \overline{H}_{(o\text{BzO}^-)_x - (m\text{BzO}^-)_x} = \delta \Delta \overline{H}_{6\,o\text{HBzO}} - \delta \Delta \overline{H}_{6\,m\text{HBzO}} + \Delta \overline{H}_{(o\text{BzO}^-)_{\text{H2O}} - (m\text{BzO}^-)_{\text{H2O}}} \qquad (7)$$

while the difference in the solvation enthalpy between the undissociated molecules is

$$\Delta \overline{H}_{(o\text{HBzO})_x - (m\text{HBzO})_x} = \delta \Delta \overline{H}_{5\,o\text{HBzO}} - \Delta \overline{H}_{5\,m\text{HBzO}} + \Delta \overline{H}_{(o\text{HBzO})_{\text{H2O}} - (m\text{HBzO})_{\text{H2O}}} \qquad (8)$$

In the same way, the differences in solvation of the couples $o\text{BzO}^-/p\text{BzO}^-$, $m\text{BzO}^-/p\text{BzO}^-$, $o\text{HBzO}/p\text{HBzO}$ and $m\text{HBzO}/p\text{HBzO}$ were calculated.

The final differences of eqns. (7) and (8) are arbitrarily assumed to be equal to zero and the resulting $\Delta \overline{H}_{(o\text{BzO}^-)_x - (m\text{BzO}^-)_x}$ and $\Delta \overline{H}_{(o\text{HBzO})_x - (m\text{HBzO})_x}$ values are plotted in Figs. 4(a) and (b) as functions of solvent composition. These values are supposed to approach very closely to the true values[2].

It is clear (Figs. 1–3) that the enthalpic term is the driving force of ionization processes.

For the *m*- and *o*-nitrobenzoic acids, the anions' desolvation plays a much more important role than the undissociated molecules' solvation.

A comparison of the curves in Fig. 4(a) seems to indicate that the *ortho* anion is solvated to a larger extent than the *meta* anion in the range of mole fraction $0.1 \leq X_{\text{DMSO}} \leq 0.8$.

No resonance interaction is to be expected in water for *o*- and *m*-nitrobenzoic acids and their anions. Indeed, in the *o*-nitro compound the $-\text{NO}_2$, $-\text{COOH}$ and $-\text{COO}^-$ groups are not in the same plane of the benzene ring[7]. Therefore, only the inductive effect is responsible for the decrease in the negative charge on the carboxylate group.

The nitrogroup in a *meta* position attracts the negative charge of the carboxylate anion more weakly than in the *ortho* position, thus allowing stronger interactions between $-\text{COO}^-$ and H_2O molecules.

For this reason, in mixtures with a low DMSO content ($X_{\text{DMSO}} < 0.1$), the *m*-nitro anion is more solvated than the *o*-nitro anion. With the increase in the DMSO content, the number of H_2O molecules decreases. As a result, the *meta* ion becomes more desolvated than the *ortho* anion.

This trend lasts until $X_{\text{DMSO}} = 0.4$–0.6 where the destabilization of the *meta* anion relative to the *ortho* anion shows a sharp maximum.

With a further increase in the DMSO content, $\Delta \overline{H}_{o\text{BzO}^-)_x - 'm\text{BzO}^-)_x}$ quickly increases, thus indicating that the solvation of the two anions becomes very similar at $X_{\text{DMSO}} = 0.8$.

This trend can be related to the diminished solvation of the carboxylate group when the solvent is changed from water to the mixed solvent.

The two $-\text{CH}_3$ interfere with the approach of the negative group to the dipole. This fact, in turn, allows the *ortho* anion to re-establish the resonance between the phenyl and carboxyl group. The effective dipole–dipole interactions with DMSO molecules stabilize the *ortho* anion. Beyond $X_{\text{DMSO}} = 0.7$ both the anions are simi-

larily desolvated, due to the large percentage of DMSO, which is itself highly associated.

As previously stated, reliable results with p-nitrobenzoic acid can be obtained only when $X_{DMSO} \geq 0.4$, but the $\Delta\bar{H}_s$ values in H_2O are reported in the literature[8].

On account of the fact that for X_{DMSO} values ranging from 0.4 to 0.8 the $\Delta\bar{H}_s$ values of p-nitrobenzoic acid are nearly constant, it is highly probable that a dramatic increase in the solvation of the undissociated molecules takes place within the range between pure water and $X_{DMSO} = 0.4$. This fact can be related to a dipolar structure that can be thought to be in resonance with an uncharged structure in the p-nitrobenzoic acid molecule. The dipole interacts effectively with the dipolar molecules of DMSO, so that the undissociated molecules are completely solvated even at low DMSO mole fraction. On the basis of the above considerations, it seemed reasonable to assume a linear trend for $\delta\Delta\bar{H}_s$ between pure water and $X_{DMSO} = 0.4$.

For the undissociated molecules the transfer tendency decreases according to the sequence pHBzO > oHBzO.

Figure 3 shows that the transfer enthalpy of the undissociated molecules plays a very important role in the dissociation of p-nitrobenzoic acid.

The negative charge on the p-nitroanion is mainly localized on the –COOH group, owing to a weak electron inductive effect. The latter, together with a resonance effect, means that the solvation effect is strongest for the p-anion. Thus the order of transfer is pBzO⁻ > oBzO⁻ in the range $0 \leq X_{DMSO} \leq 0.7$.

At $X_{DMSO} = 0.8$, the *ortho* and *para* anions display an inversion of solvation enthalpy.

It is interesting to note that, with respect to enthalpy solvation, the o-nitro anion behaves in an opposite way to the o-chloro anion[1].

At $X_{DMSO} = 0.3$–0.4, the minimum[9] for the so called *ortho-* effect ($pK_p - pK_o$) can be related to the minimum in the relative enthalpy solvation for *ortho* and *para* anions.

The differences in solvation enthalpy for the anions are most marked at $X_{DMSO} = 0.5$ where maximum solvating power is displayed[10, 11].

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