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CALORIMETRIC STUDY OF IONIZATION PROCESSES FOR NITRO-SUBSTITUTED PHENOLS IN WATER–DIMETHYLSULFOXIDE MIXTURES AT 25°C

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ABSTRACT

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

The different solvation values obtained for *ortho*-nitrophenol with respect to the *meta* and *para* isomers, were explained taking into account the electrostatic forces between the water molecules and the anions, as well as the intramolecular and intermolecular hydrogen bonds associated with the undissociated molecules.

INTRODUCTION

The ionization of chloro-benzoic isomers in water–dimethylsulfoxide (DMSO) mixtures and the related thermodynamic quantities have been the subject of a recent research in our laboratory[1]. The different results obtained for the three acids were explained taking account of the different effects displayed on the solvation and ionization phenomena by the clorine atom at the various positions in the aromatic ring.

In the present research, we examinate the behaviour of other simple disubstituted benzene derivatives, in which the position of the substituent groups could possibly give intermolecular and intramolecular hydrogen bond: the nitrophenol isomers.

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus has been described previously[1]. DMSO (Carlo Erba, RP grade) was purified according to Butler's procedure[2].

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 1N HCl and 0.1N NaOH were prepared from standard solutions; their concentrations were checked by potentiometric titrations. *m*-Nitrophenol (K & K) was distilled under reduced pressure, *o*-nitrophenol was purified by steam distillation and *p*-nitrophenol was purified by crystallization from water–alcohol mixtures. The m.p. of the phenols were checked before use; subsequently, these compounds were stored in a vacuum desiccator on P_2O_5. The ΦO_sNa solutions (where subscript s indicates the substituted phenols) were prepared by adding an amount of NaOH solution, containing approximately one equivalent of alkali, to *o*-, *m*- and *p*-nitrophenol 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 phenol, about 4 or 5% of the original content, was not converted to salt and remained as free phenol, to avoid the presence of free alkali.

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

$$(\Phi O_sH)_X \rightarrow (\Phi O_s^-)_X + (H^+)_X \tag{1}$$

The molar enthalpy of ionization of ΦO_sH $\overline{\Delta H}_1$ was obtained, as previously described[1], by the experimental measurement of:

The molar enthalpy of reaction ($\overline{\Delta H}_2$) of the sodium salts ΦO_sNa, dissolved in the mixed solvent of X' mole fraction, with 1N HCl

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

The molar enthalpy of dilution ($\overline{\Delta H}_3$) of the same amount of 1N 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[3] and the substituted phenols[4], it can also be inferred that the salts undergo, in the most unfavourable case (m-ΦO_sH at $X_{DMSO} = 0.8$), an hydrolysis $\beta < 0.037$ with an error of 0.26%, while the precision limit of our measurements are at best 0.6%.

The two values $\overline{\Delta H}_3$ and $\overline{\Delta H}_2$ were algebraically subtracted so that $\overline{\Delta H}_4 = \overline{\Delta H}_3 - \overline{\Delta H}_2$ is the thermal effect of the hypothetical process represented as

$$(\Phi O_sH)_X + (Na^+)_X \rightarrow (\Phi O_s^-)_{X'} + (Na^+)_{X'} + (H^+)_X \tag{4}$$

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 ΦO_sNa (at infinite dilution) from solvent X' to solvent X. The transfer process can be described as

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

process (1) being the sum of processes (4) and (5).

It has to be remarked that the difference ($X' - X$) turns out to be very small for each couple: in the most unfavourable case it was $2 \cdot 10^{-4}$, when the DMSO final mole fraction was 0.8.

For the transfer enthalpy of Na^+ and ΦO_s^- of the *o*-, *m*- and *p*-nitrophenol, an average variation of 1.57 kcal mol^{-1}, 3.56 kcal mol^{-1} and 4.46 kcal mol^{-1} are observed, when the mole fraction of the solvent mixture was varied by 0.1 unit. These values were calculated by using the experimental measurements published in this work. The error introduced by neglecting the thermal effect of process (5) is, respectively for *o*-, *m*- and *p*-nitrophenol 0.014, 0.02 and 0.037%. Therefore, we take the $\bar{\Delta H}_4$ of reaction (4) as the molar enthalpy of ionization ($\bar{\Delta H}_1$) of substituted phenols dissolved in DMSO–water solutions at 25°C. We did not extend our measurements beyond $X_{DMSO} = 0.8$ mainly because the difference between X' and X would have been too large for the approximation mentioned above.

For every one of the water–DMSO mixtures at X_{DMSO} mole fraction, these $\bar{\Delta H}_1$ values refer to the ionization process of one mole of $\Phi O_s H$, dissolved at infinite dilution in the mixed solvent, yielding one mole of protons and one mole of ΦO_s^- ions solvated in the same solvent.

In order to refer process (1) to one initial standard state only, we measured the solution enthalpy of the crystalline nitrophenols ($\bar{\Delta H}_6$) in water–DMSO mixtures at various mole fraction:

$$\Phi O_s H_{cr} \rightarrow (\Phi O_s H)_X \tag{6}$$

therefore the process

$$\Phi O_s H_{cr} \rightarrow (H^+)_X + (\Phi O_s^-)_X \tag{7}$$

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 $2 \cdot 10^{-3}$ to $4 \cdot 10^{-3}$ F were used. Therefore, the $\bar{\Delta H}_1$ and $\bar{\Delta H}_6$ values can be considered at infinite dilution[5].

The enthalpy value, at $X_{DMSO} = 0$, of process (6) for *o*-nitrophenol was not measured, but found in the literature[6], because the dissolution of this compound is very slow and our apparatus could not record the enthalpic effect accurately.

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

RESULTS

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

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[4] the $pK_{a/1}$ values of process (1) at 20°C are reported for *o*-, *m*-

TABLE 1

MOLAR ENTHALPY OF IONIZATION ($\overline{\Delta H}_1$) AND SOLUTION ($\overline{\Delta H}_6$) FOR *o*-NITROPHENOL 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})	$\overline{\Delta H}_7$ (kcal mol^{-1})
0	4.55 ± 0.02	6.31	10.86
0.1	5.32 ± 0.03	7.00 ± 0.02	12.32 ± 0.04
0.2	6.98 ± 0.04	7.10 ± 0.01	14.08 ± 0.04
0.3	9.33 ± 0.05	5.10 ± 0.02	14.43 ± 0.05
0.4	10.29 ± 0.06	5.01 ± 0.01	15.30 ± 0.06
0.5	13.19 ± 0.08	3.98 ± 0.02	17.17 ± 0.08
0.6	16.15 ± 0.09	3.81 ± 0.01	19.97 ± 0.09
0.7	18.64 ± 0.1	3.01 ± 0.01	21.67 ± 0.1
0.8	21.70 ± 0.12	2.98 ± 0.01	24.68 ± 0.12

TABLE 2

MOLAR ENTHALPY OF IONIZATION ($\overline{\Delta H}_1$) AND SOLUTION ($\overline{\Delta H}_6$) FOR *m*-NITROPHENOL 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})	$\overline{\Delta H}_7$ (kcal mol^{-1})
0	4.90 ± 0.02	5.21 ± 0.03	10.11 ± 0.04
0.1	6.00 ± 0.03	6.08 ± 0.02	12.08 ± 0.04
0.2	6.38 ± 0.03	6.75 ± 0.02	13.13 ± 0.04
0.3	14.71 ± 0.08	6.68 ± 0.02	21.39 ± 0.08
0.4	16.53 ± 0.09	2.83 ± 0.01	19.35 ± 0.09
0.5	24.62 ± 0.13	2.06 ± 0.01	26.69 ± 0.13
0.6	21.40 ± 0.11	1.57 ± 0.01	22.97 ± 0.11
0.7	22.35 ± 0.12	1.19 ± 0.02	23.54 ± 0.12
0.8	30.32 ± 0.13	0.84 ± 0.01	31.16 ± 0.13

TABLE 3

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

X_{DMSO}	$\overline{\Delta H}_1$ (kcal mol^{-1})	$\overline{\Delta H}_6$ (kcal mol^{-1})	$\overline{\Delta H}_7$ (kcal mol^{-1})
0	4.65 ± 0.03	4.29 ± 0.02	8.94 ± 0.04
0.1	5.61 ± 0.03	5.48 ± 0.02	11.09 ± 0.04
0.2	9.06 ± 0.04	5.17 ± 0.01	14.23 ± 0.04
0.3	11.44 ± 0.06	4.34 ± 0.01	15.79 ± 0.06
0.4	22.22 ± 0.12	2.13 ± 0.02	24.35 ± 0.12
0.5	25.04 ± 0.14	1.10 ± 0.01	26.14 ± 0.14
0.6	18.17 ± 0.09	0.62 ± 0.009	18.79 ± 0.09
0.7	25.29 ± 0.12	0.14 ± 0.006	25.47 ± 0.12
0.8	24.03 ± 0.13	−0.14 ± 0.009	23.89 ± 0.13

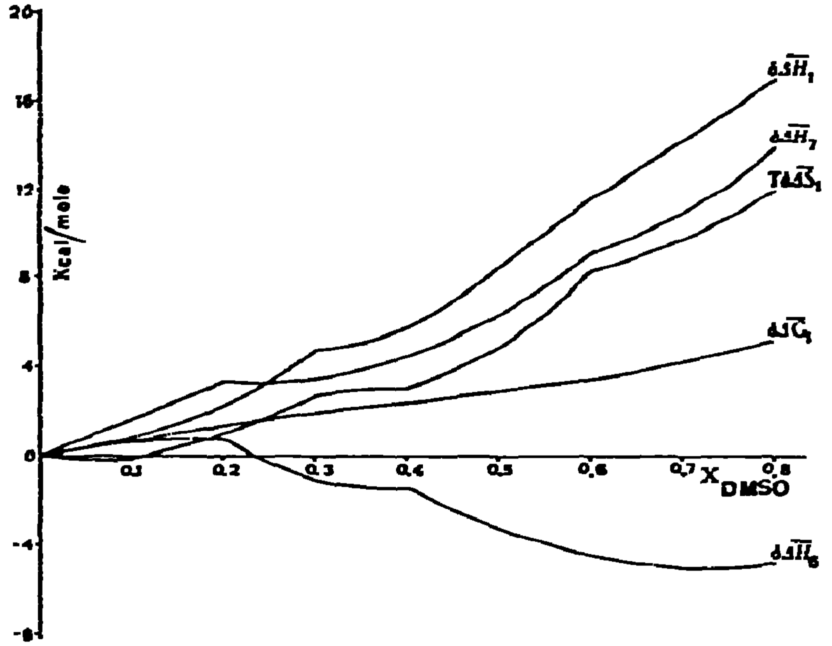


Fig. 1. Thermodynamic quantities for the transfer of the *o*-nitrophenol from pure water to DMSO–water mixtures, as function of the mole fraction at 25°C.

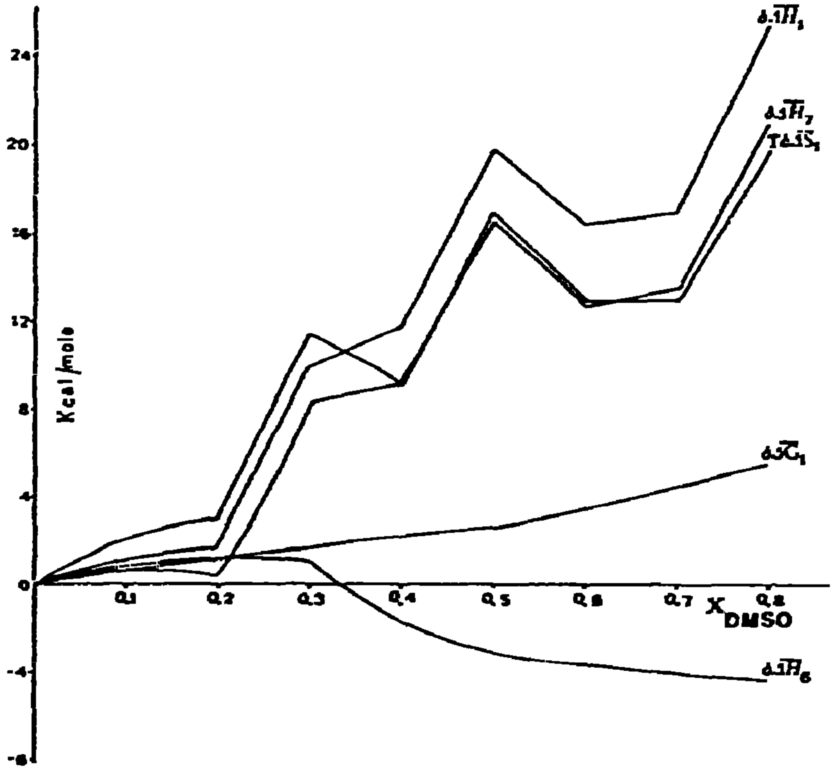


Fig. 2. Thermodynamic quantities for the transfer of the *m*-nitrophenol from pure water to DMSO–water mixtures, as function of the mole fraction at 25°C.

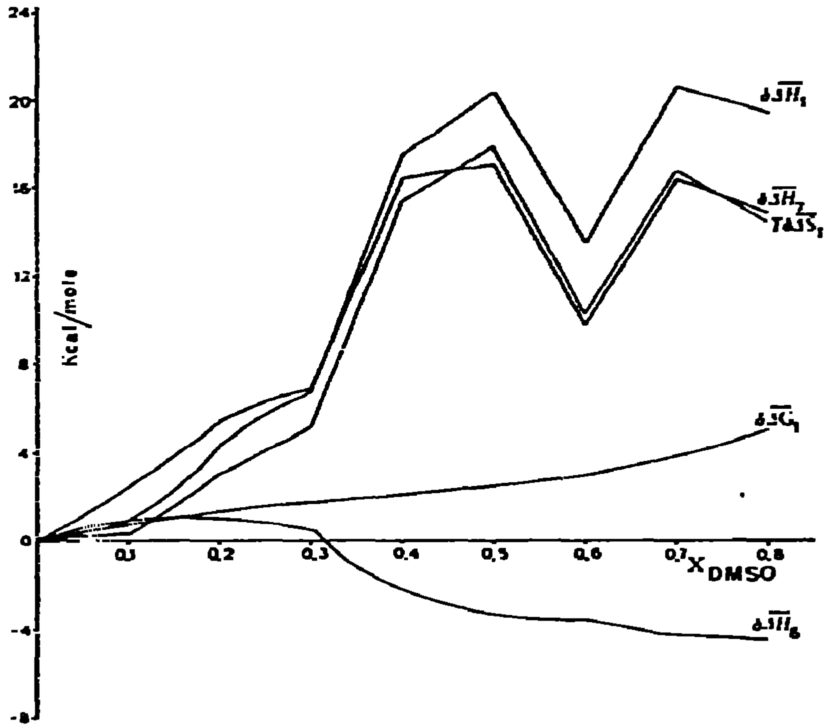


Fig. 3. Thermodynamic quantities for the transfer of the *p*-nitrophenol from pure water to DMSO-water mixtures, as function of the mole fraction at 25 °C.

and *p*-nitrophenol. 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

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

From $pK_{a/1}$ at 25°C, we calculated the free energy $\overline{\Delta G}_1$ relative to process (1), and the $T\Delta S_1$ values through the Gibbs-Helmholtz equation.

For comparison, it is convenient to express the ionization enthalpy $\overline{\Delta H}_1$ of the nitro-substituted phenols 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 the ionization process, while $\delta\overline{\Delta H}_6$ and $\delta\overline{\Delta H}_7$ values represent the transfer enthalpy of the undissociated molecule and of the two ions H^+ and ΦO_s^-, respectively, from pure water to the mixed solvent. All these data are plotted against X_{DMSO} in Figs. 1, 2 and 3.

DISCUSSION

From the curves of Fig. 1, it can be inferred that, from the enthalpic point of view, the desolvation of the *o*-ΦO^- anion plays a much more important role than the solvation of the undissociated molecule (H^+ ions are always better solvated in water–DMSO mixtures than in pure water)[7–9]. With respect to this point, *o*-nitrophenol and *o*-chlorobenzoic acid[1] behave in the same way.

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 process (1).

The $\delta\overline{\Delta H}_1$ values are larger than the corresponding $\delta\overline{\Delta G}_1$ and $T\delta\overline{\Delta S}_1$ values. Thus the enthalpic term can be reasonably identified with the driving force of the process.

A comparison of Figs. 1, 2 and 3 suggests that *m*- and *p*-nitrophenol, from the enthalpic point of view, undergo ionization with much greater difficulty than *o*-nitrophenol, so that *m*- and *p*-nitrophenols and *m*- and *p*-chlorobenzoic acids[1] display an opposite behaviour. This fact can be ascribed to the different solvation which the molecules and the ions of the three nitrophenols undergo in the solvent mixture.

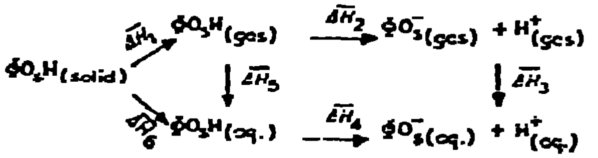
It may be interesting, therefore, to compare the solvation enthalpies of the three anions $o\Phi O^-$, $m\Phi O^-$ and $p\Phi O^-$, for each of the DMSO-water mixtures considered, using the transfer enthalpy values of the couples $H^+/o\Phi O^-$ $H^+/m\Phi O^-$ and $H^+/p\Phi O^-$. In the various solvent mixtures, the differences in the solvation enthalpy between the solvated nitroanions were calculated as[1]

$$\begin{aligned}
\overline{\Delta H}_{(o\Phi O^-)_x-(m\Phi O^-)_x} &= \delta\overline{\Delta H}_{7o\Phi OH} - \delta\overline{\Delta H}_{7m\Phi OH} + \overline{\Delta H}_{(o\Phi O^-)_{H_2O}-(m\Phi O^-)_{H_2O}}\\
\overline{\Delta H}_{(o\Phi O^-)_x-(p\Phi O\ )_x} &= \delta\overline{\Delta H}_{7o\Phi OH} - \delta\overline{\Delta H}_{7p\Phi OH} + \overline{\Delta H}_{(o\Phi O^-)_{H_2O}-(p\Phi O^-)_{H_2O}} \qquad (8)\\
\overline{\Delta H}_{(m\Phi O^-)_x-(p\Phi O^-)_x} &= \delta\overline{\Delta H}_{7m\Phi OH} - \delta\overline{\Delta H}_{7p\Phi OH} + \overline{\Delta H}_{(m\Phi O^-)_{H_2O}-(p\Phi O^-)_{H_2O}}
\end{aligned}$$

On the other hand, the differences between the transfer enthalpy of the undissociated molecules of *o*-, *m*- and *p*-nitrophenol, represent the differences of the solvation enthalpy between the molecules, in the various solvent mixtures, less the differences (which are constant) between the hydration enthalpies of these molecules in pure water:

$$\begin{aligned}
\overline{\Delta H}_{(o\Phi OH)_x-(m\Phi OH)_x} &= \delta\overline{\Delta H}_{6o\Phi OH} - \delta\overline{\Delta H}_{6m\Phi OH} + \overline{\Delta H}_{(o\Phi OH)_{H_2O}-(m\Phi OH)_{H_2O}}\\
\overline{\Delta H}_{(o\Phi OH)_x-(p\Phi OH)_x} &= \delta\overline{\Delta H}_{6o\Phi OH} - \delta\overline{\Delta H}_{6p\Phi OH} + \overline{\Delta H}_{(o\Phi OH)_{H_2O}-(p\Phi OH)_{H_2O}} \qquad (9)\\
\overline{\Delta H}_{(m\Phi OH)_x-(p\Phi OH)_x} &= \delta\overline{\Delta H}_{6m\Phi OH} - \delta\overline{\Delta H}_{6p\Phi OH} + \overline{\Delta H}_{(m\Phi OH)_{H_2O}-(p\Phi OH)_{H_2O}}
\end{aligned}$$

By putting the last differences arbitrarily equal to zero, eqns (8) and (9) are plotted in Figs. 4a and 4b versus the solvent composition. But it is possible to calculate the $\overline{\Delta H}_{(m\Phi O^-)_{H_2O}-(p\Phi O^-)_{H_2O}}$ and $\overline{\Delta H}_{(m\Phi OH)_{H_2O}-(p\Phi OH)_{H_2O}}$ values using the scheme



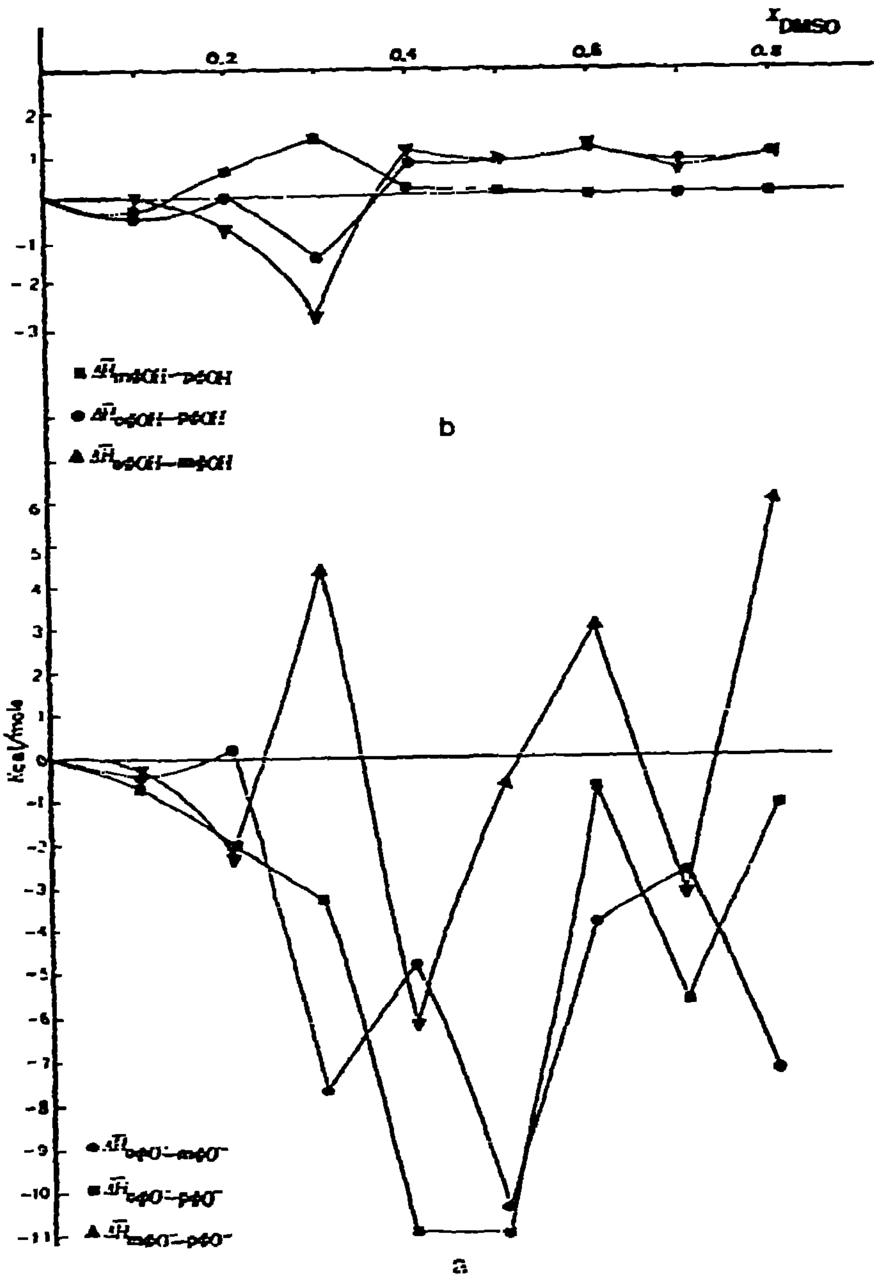


Fig. 4. Differences in the solvation enthalpy between (a) the nitroanion couples and (b) between the undissociated nitro-molecule couples, in various DMSO-water mixtures. The differences in the hydration enthalpy both between the anion couples and between the undissociated molecule couples are arbitrarily set equal to zero.

where $\Delta\bar{H}_1$, $\Delta\bar{H}_6$ and $\Delta\bar{H}_4$ represent the enthalpies of sublimation[10], solution (this work) and ionization (this work), respectively, for *meta*- and *para*-phenols.

The enthalpies of hydration ($\Delta\bar{H}_5$) of *meta* and *para* molecules, as well as their difference, were calculated from the corresponding sublimation and solution enthalpies: $\Delta\bar{H}_1 + \Delta\bar{H}_5 = \Delta\bar{H}_6$. The extent of the difference in the hydration enthalpies of the *meta*- and *para*-phenol anions can be estimated by a combination of the enthalpies of hydration ($\Delta\bar{H}_5$) and ionization ($\Delta\bar{H}_4$) of the undissociated molecules: $\Delta\bar{H}_2 + \Delta\bar{H}_3 = \Delta\bar{H}_5 + \Delta\bar{H}_4$. The contribution to $\Delta\bar{H}_3$ from the hydration of the proton is independent of ΦO_x and $\Delta\bar{H}_2$ is probably fairly insensitive to the nature of the *meta* and *para* substituent. Thus, the difference between $\Delta\bar{H}_5 + \Delta\bar{H}_4$ for *meta*- and *para*-phenols will reflect the difference between the enthalpies of hydration of the phenol anions. The (very small) figures are 0.03 kcal mol^{-1} for $\Delta\bar{H}_{(m\Phi OH)_{H_2O}-(p\Phi OH)_{H_2O}}$ and 0.31 kcal mol^{-1} for $\Delta\bar{H}_{(m\Phi O^-)_{H_2O}-(p\Phi O^-)_{H_2O}}$.

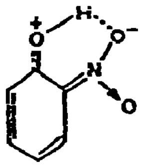
It seemed reasonable to assume similar values for the differences between the enthalpies of hydration $\Delta\bar{H}_{(o\Phi O^-)_{H_2O}-(m\Phi O^-)_{H_2O}}$, $\Delta\bar{H}_{(o\Phi O^-)_{H_2O}-(p\Phi O^-)_{H_2O}}$, $\Delta\bar{H}_{(o\Phi OH)_{H_2O}-(m\Phi OH)_{H_2O}}$ and $\Delta\bar{H}_{(o\Phi OH)_{H_2O}-(p\Phi OH)_{H_2O}}$ so that the values plotted in Figs. 4a and 4b should approach very closely the true values. Figure 4a shows that the transfer of the nitro anions from pure water to DMSO–water mixtures decreases according to the sequence $o\Phi O^- > m\Phi O^- > p\Phi O^-$ except in the ranges from 0.25 to 0.35 and from 0.53 to 0.65, where $p\Phi O^- > m\Phi O^-$.

Owing to the resonance between the phenolate oxygen and the oxygens in the neighbouring nitro group in the *ortho* ion, the electrostatic force between the water molecules and the *ortho* anion is much greater than in *para* and *meta* anions. Therefore, the latter anions are much more affected by the drastic decrease in the H_2O/DMSO molar ratio from 9 : 1 at $X_{DMSO} = 0.1$ to 2.3:1 at $X_{DMSO} = 0.3$.

In the range from 0.0 to 0.15 the transfer of the undissociated molecules decreases according to the sequence $o\Phi OH > m\Phi OH > p\Phi OH$ while from 0.15 to 0.38 the following order is observed $o\Phi OH > p\Phi OH > m\Phi OH$.

Beyond the 0.38 molar ratio, the sequence is $p\Phi OH \cong m\Phi OH > o\Phi OH$.

It is possible to admit[4] that the *ortho* form can be in resonance with the cyclic dipolar structure (I), which is stable mostly in water-rich mixtures where dipole–dipole interactions



(I)

are allowed with the water molecules, so that the *ortho* molecule is more solvated than *para* and *meta* isomers. When the DMSO content in the solvent mixture is increased, DMSO competes with the nitro group for the phenolic proton, the chelate ring structure is broken and the nitro group is forced out of the ring plane; owing to this reason, the molecule interacts with DMSO by some weak specific interaction. Therefore, beyond 0.37 mole fraction, the *ortho* molecule is less solvated than *para* and *meta* isomers.

We think that the increase in $\Delta\bar{H}_1$ values observed, when water is progressively substituted by DMSO, can be related more to the anions desolvation rather than to the solvation of undissociated molecules. Therefore, unlike the *ortho* isomer, the ΔH_1 curves for both *meta* and *para* molecules show a sharp rise beyond 0.2 mole fraction.

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