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THERMODYNAMICS OF THE IONIZATION PROCESS OF PHENOL IN WATER–DIMETHYLSULFOXIDE MIXTURES AT 25°C

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ABSTRACT

The ionization and solution enthalpies of phenol were measured calorimetrically at 25°C in water–DMSO mixtures ranging from pure water to 0.8 mole fraction of DMSO. The ΔG^0 values for the ionization process were calculated in the same solutions. The weak acidity of phenol is explained on the basis of the poor resonance effect of the phenate anion in water–DMSO solutions.

INTRODUCTION

The ionization of nitro-phenol isomers in water–dimethylsulfoxide (DMSO) mixtures and the related thermodynamic quantities have been the subject of research in our laboratory [1]. In the present work, the behavior of the ionization of phenol is examined. This compound is very important since it may be used as a reference in some free energy linear relationships both in the gaseous and liquid phase [2,3].

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus has been described previously [4]. In the present work the thermograms were read using a computer program and the experimental values were obtained using a different technique which will be the subject of further work.

The DMSO–water mixtures were prepared by weight from purified DMSO and CO_2-free twice-distilled water. Aqueous solutions of 1 N HCl and 0.1 N NaOH were prepared from standard solutions; their concentrations were checked by potentiometric titrations. The phenol (K&K) was recrystallized from water–alcohol mixtures to constant melting point.

Solutions of phenol (PhOH) in DMSO were prepared in a nitrogen-filled dry box. Solutions of PhONa were prepared by successive dilution of a stock solution of phenol and by adding NaOH solution of known molarity to the phenol dissolved in the mixed solvent. As a result of these operations 100 g of the DMSO–water solution at X mole fraction were obtained. The concentration of the sodium salt was always in the range 2×10^{-3}–4×10^{-3} m (molal). Approximately 4 or 5% of the original phenol content was not converted to the salt and remained as free phenol in order to avoid the presence of free alkali and to repress the hydrolysis.

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

$$(\mathrm{PhOH})_X \rightarrow (\mathrm{PhO}^-)_X + (\mathrm{H}^+)_X \tag{1}$$

The molar enthalpy of ionization, $\Delta \overline{H}_1$, of PhOH was obtained as described previously [1,4] by the experimental measurement of:

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

$$(\mathrm{PhO}^-)_{X'} + (\mathrm{Na}^+)_{X'} + (\mathrm{H}^+)_{\mathrm{aq}} + (\mathrm{Cl}^-)_{\mathrm{aq}} = (\mathrm{PhOH})_X + (\mathrm{Na}^+)_X + (\mathrm{Cl}^-)_X \tag{2}$$

(b) The molar enthalpy of dilution, $\Delta \overline{H}_3$, of the same amount of 1 N HCl in the same solvent mixture at X' mole fraction

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

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

From the values of the dissociation constants of water [5] and phenol [6] it can also be inferred that the salt undergoes, in the most unfavorable case ($X_{\mathrm{DMSO}} = 0.8$), hydrolysis with $\beta < 0.01\%$. Therefore, it is not necessary to correct the $\Delta \overline{H}_2$ values measured experimentally in process (2) for hydrolysis.

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

$$(\mathrm{PhO}^-)_{X'} + (\mathrm{Na}^+)_{X'} \rightarrow (\mathrm{PhO}^-)_X + (\mathrm{Na}^+)_X \tag{4}$$

The difference (X'–X) turns out to be 2×10^{-4} in the most unfavorable case ($X_{\mathrm{DMSO}} = 0.8$).

The thermal effect of process (4) was calculated using the experimental measurements published in this work. For each of the water–DMSO mixtures at X_{DMSO} mole fraction, the $\Delta \overline{H}_1$ values refer to the ionization of one mole of PhOH, dissolved at infinite dilution in 1000 g of the mixed solvent, yielding one mole of protons and one mole of PhO^- ions solvated in the same amount of solvent. In order to refer process (1) to one initial thermodynamic state only, the solvation enthalpies of the crystalline phenol, $\Delta \overline{H}_s$ were measured in the various solvent mixtures

$$PhOH_{cr} \rightarrow (PhOH)_X \qquad (5)$$

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

$$PhOH_{cr} \rightarrow (H^+)_X + (PhO^-)_X \qquad (6)$$

refer to an identical initial thermodynamic state.

In (1), and (5), concentrations ranging from 2×10^{-3} to 4×10^{-3} m were used; therefore, the $\Delta\overline{H}$ values related to these processes were assumed to be equal to the ΔH^0 [7] values. All the measurements were carried out at 25°C, the average thermal jump in the cell during the experiments being about 2×10^{-3}°C.

RESULTS

Table 1 shows the ΔH^0 values of processes (1), (5) and (6) obtained for phenol in DMSO–water solutions as functions of the DMSO mole fraction.

In the literature the $pK_{a/1}$ values of process (1) at 20°C are reported for phenol at various mole fractions of DMSO. From these data and the ΔH_1^0 values reported in Table 1, the $pK_{a/1}$ values at 25°C are calculated using the well-known equation

$$pK_{25^\circ C} = pK_{20^\circ C} - \frac{\Delta H_1^0 \Delta T}{1.987 \times 2.303\ T_1 T_2}$$

From $pK_{a/1}$ at 25°C the free energy, ΔG_1^0, is calculated relative to process (1) and the Gibbs–Helmholtz equation is used for the values of $T\Delta S_1$. For comparison it is convenient to express the ionization enthalpy values, ΔH_1^0,

TABLE 1

Molar enthalpy of ionization (ΔH_1^0) and solution (ΔH_5^0) of phenol in DMSO–water solutions of various mole fractions at 25°C

X_{DMSO}	ΔH_1^0 (kcal mole^{-1})	ΔH_5^0 (kcal mole^{-1})	ΔH_6^0 (kcal mole^{-1})
0.0	5.48	3.01	8.49
0.1	8.00	3.41	11.41
0.2	12.97	3.13	16.10
0.3	13.98	2.21	16.18
0.4	17.56	1.18	18.73
0.5	26.40	0.38	26.79
0.6	17.74	−0.13	17.61
0.7	16.08	−0.41	15.67
0.8	20.29	−0.58	19.71

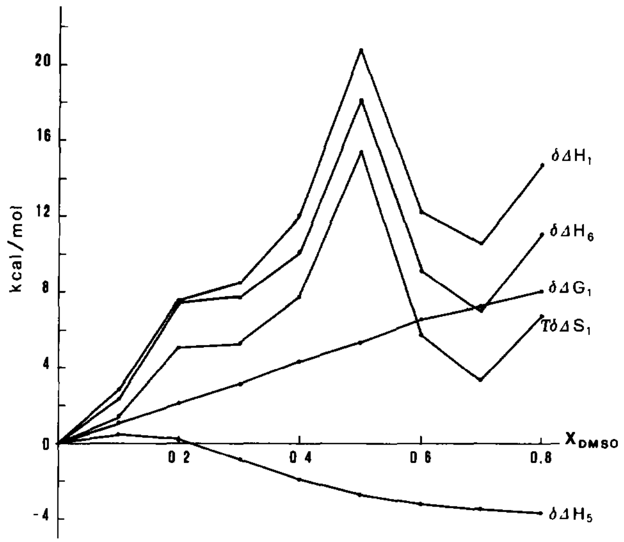

Fig. 1. Thermodynamic quantities for the transfer of phenol from pure water to DMSO–water mixtures as a function of the mole fraction at 25°C.

of phenol as the difference between the values obtained in the mixed solvent at X mole fraction and those obtained in pure water, so that

$$\delta\Delta H_1^0 = \left(\Delta H_1^0\right)_X - \left(\Delta H_1^0\right)_{X=0}$$

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 process, while $\delta\Delta H_5^0$ and $\delta\Delta H_6^0$ represent the transfer enthalpy of the undissociated molecule and the two ions H^+ and PhO^-, respectively, from pure water to mixed solvent. All these data are plotted against X_{DMSO} in Fig. 1.

DISCUSSION

From the curve of Fig. 1 it can be inferred that the enthalpic term can be identified with the driving force of process (1) mostly around $X_{DMSO} = 0.5$. Furthermore, the desolvation of the anion PhO^- plays a much more important role than that of the undissociated molecule. It may be interesting, therefore, to compare the solvation enthalpies of the phenate anion, PhO^-, with the benzoic anion, $PhCOO^-$, for each of the DMSO–water mixtures considered, using the transfer enthalpy values. As previously shown [1], the difference in solvation enthalpy between the solvated anions is calculated as

$$\Delta H^0_{(PhO^-)_X-(PhCOO^-)_X} = \delta\Delta H^0_{(6PhOH)} - \delta\Delta H^0_{(6PhCOOH)} + \Delta H^0_{(PhO^-)_{aq}-(PhCOO^-)_{aq}} \quad (7)$$

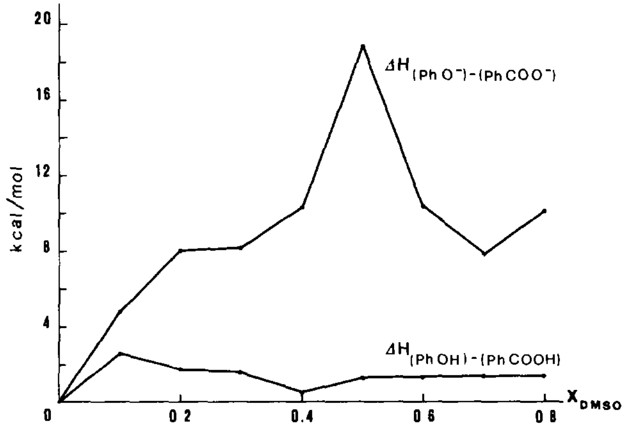

Fig. 2. Differences in the solvation enthalpies between the anions and the undissociated molecules of phenol and benzoic acid, in various DMSO–water mixtures. The differences in the hydration enthalpies both between the anion couples and between the undissociated molecule couples are arbitrarily set equal to zero.

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

$$\Delta H^0_{(\mathrm{PhOH})_x\text{-}(\mathrm{PhCOOH})_x} = \delta\Delta H^0_{5(\mathrm{PhOH})} - \delta\Delta H^0_{5(\mathrm{PhCOOH})} + \Delta H^0_{(\mathrm{PhOH})_{aq}\text{-}(\mathrm{PhCOOH})_{aq}} \tag{8}$$

The last term on the right-hand sides of eqns. (7) and (8) was arbitrarily assumed to be equal to zero and the resulting $\Delta H^0_{(\mathrm{PhO}^-)_x\text{-}(\mathrm{PhCOO}^-)_x}$ and $\Delta H_{(\mathrm{PhOH})_x\text{-}(\mathrm{PhCOOH})_x}$ values are plotted in Fig. 2 as a function of solvent composition. Both the anions and the undissociated molecules of phenol are more desolvated than those of benzoic acid.

It is clear that the difference in solvation for the anions plays a very important role in the differentiation of the acidities of phenol and benzoic acid. This fact can also be studied by comparing the solvation enthalpies of the phenate ion with those of the nitrophenol anions. The differences are calculated as

$$\Delta H^0_{(\mathrm{PhO}^-)\text{-}(o\text{-},m\text{-},p\text{-}\mathrm{PhO}^-)} = \delta\Delta H^0_{6(\mathrm{PhOH})} - \delta\Delta H^0_{6(o\text{-},m\text{-},p\text{-}\mathrm{PhOH})} + \Delta H^0_{(\mathrm{PhO}^-)\text{-}(o\text{-},m\text{-},p\text{-}\mathrm{PhO}^-)}$$

and are plotted in Figs. 3–5 as a function of the solvent composition. From these Figs. it can be observed that the *ortho*-nitro anion is much more solvated than the unsubstituted anion in almost the whole mole fraction range, while for the *para*- and *meta*-anions this is true only in the water-rich solutions. This behavior confirms [1] that the large electrostatic force between the water molecules and the *ortho*-anion is due, in turn, to the great

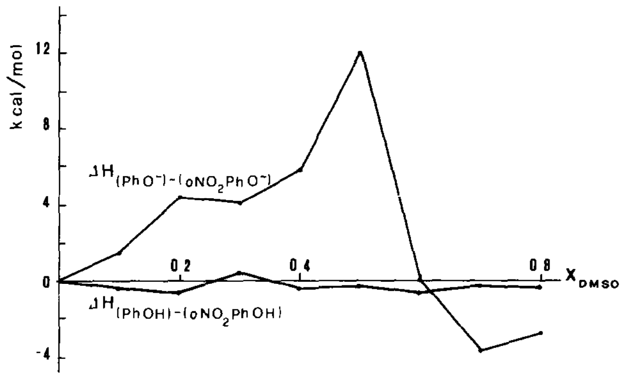

Fig. 3. Differences in the solvation enthalpies between the anions and the undissociated molecules of phenol and *o*-nitro-phenol in various DMSO–water mixtures. The differences in the hydration enthalpies both between the anion couples and between the undissociated molecule couples are arbitrarily set equal to zero.

resonance between the phenolate oxygen and the oxygens in the neighbouring nitrogroup. It is clear that the relative stabilization of the anion with respect to the undissociated molecule is less effective for phenol than for benzoic acid and nitro-phenol derivatives. It is well known that the anions polarize the solvent molecules and the degree of this polarization strictly correlates with the stabilization of the anions. Thus the *ortho*-anion stabilizes itself by dispersing its charge and surrounding itself with water molecules. Beyond $X_{DMSO} = 0.6$ this is not possible because of the high DMSO content. Indeed the electrostatic energy of the anions decreases as the dielectric constant of the solvent increases. Thus we can conclude that the poor resonance effect of the anion is the principal cause of the weak acidity of phenol in water–DMSO solutions.

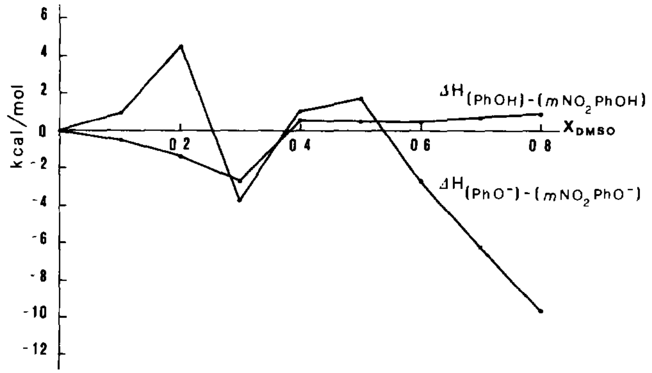

Fig. 4. Differences in the solvation enthalpies between the anions and the undissociated molecules of phenol and *m*-nitro-phenol in various DMSO–water mixtures. The differences in the hydration enthalpies both between the anion couples and between the undissociated molecule couples are arbitrarily set equal to zero.

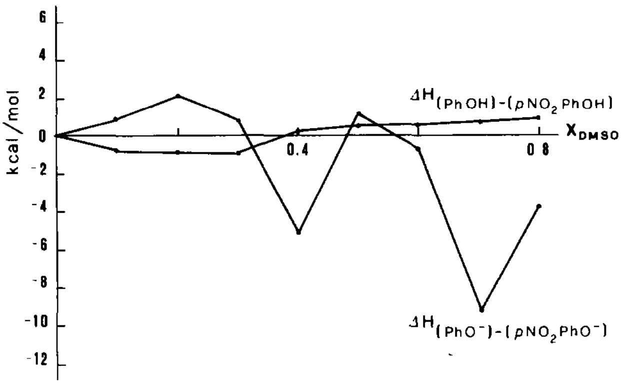

Fig. 5. Differences in the solvation enthalpies between the anions and the undissociated molecules of phenol and *p*-nitro-phenol in various DMSO–water mixtures. The differences in the hydration enthalpies both between the anion couples and between the undissociated molecule couples are arbitrarily set equal to zero.

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