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Note

Ionization thermodynamics of nitrobenzoic acids in water-DMF mixtures

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Abstract

The ionization enthalpies of *p*-, *m*- and *o*-nitrobenzoic acid were measured calorimetrically at 298.15 K in water-DMF mixtures ranging from pure water to 70% DMF by weight. The ionization entropies were calculated based on the free energy values obtained from experiments. The results were interpreted in terms of solute-solvent interactions and different substituent effects.

Keywords: DMF; Heat of ionization; Nitrobenzoic acid

1. Introduction

The ionization thermodynamic properties of nitrobenzoic acids in water-DMSO and water-ethanol mixtures have been studied extensively [1-3]. The difference in behaviour between *o*-, *m*- and *p*-nitrobenzoic acid can be related to the different solute-solvent interactions by the nitro group at the various positions on the aromatic ring. The present work reports the calorimetric measurements of the heats of ionization of these organic acids in water-DMF mixtures.

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2. Experimental

The heats of ionization of three nitrobenzoic acids (*p*-, *m*- and *o*-) were calculated indirectly from the heats of libration of these acids from the corresponding sodium salt solutions measured in an LKB BioActivity Monitor (calorimeter) at 298.15 K. The details of the experiment have been described previously [4].

The acids were purified by double recrystallization from water–alcohol mixtures, their melting points were checked before use. Water–DMF mixtures were prepared by weight from purified DMF and twice-distilled water. The weight fraction of DMF in the mixtures ranged from 0.0 to 0.7.

The calculated heats of ionization at different concentrations include the effects of ionic interactions. Duplicate runs at five different salt concentrations for each acid were carried out and extrapolated graphically to obtain the heats of ionization at infinite dilution ($\Delta H_i^\ominus$) for the acids concerned.

3. Results

Tables 1–3 show the enthalpy values of the three nitrobenzoic acids in eight water–DMF mixtures at infinite dilution, and the corresponding free energy and entropy values calculated are also tabulated.

Table 1
Thermodynamic functions of ionization of *p*-nitrobenzoic acids in water–DMF mixtures at 298.15 K

W_{DMF}	X_{DMF}	$\Delta G_i^\ominus/(\mathrm{kJ\ mol^{-1}})$	$\Delta H_i^\ominus/(\mathrm{kJ\ mol^{-1}})$	$\Delta S_i^\ominus/(\mathrm{J\ mol^{-1}})$
0	0.000	19.524	1.030	−62.029
10	0.027	20.608	0.984	−65.821
20	0.058	21.921	1.066	−69.950
30	0.096	23.406	1.140	−74.680
40	0.141	25.290	1.286	−80.509
50	0.198	27.630	1.429	−87.879
60	0.270	30.599	1.910	−96.223
70	0.356	34.138	3.511	−102.723

Table 2
Thermodynamic functions of ionization of *o*-nitrobenzoic acids in water–DMF mixtures at 298.15 K

W_{DMF}	X_{DMF}	$\Delta G_i^\ominus/(\mathrm{kJ\ mol^{-1}})$	$\Delta H_i^\ominus/(\mathrm{kJ\ mol^{-1}})$	$\Delta S_i^\ominus/(\mathrm{J\ mol^{-1}})$
0	0.000	12.673	−10.084	−76.329
10	0.027	13.872	−8.391	−74.670
20	0.058	15.242	−7.330	−75.708
30	0.096	16.955	−5.453	−75.156
40	0.141	19.010	−4.549	−79.071
50	0.198	21.522	−2.896	−81.898
60	0.270	24.776	−0.841	−85.921
70	0.356	28.601	1.643	−90.417

Table 3
Thermodynamic functions of ionization of *m*-nitrobenzoic acids in water–DMF mixtures at 298.15 K

W_{DMF}	X_{DMF}	$\Delta G_i^\ominus/(\mathrm{kJ\ mol^{-1}})$	$\Delta H_i^\ominus/(\mathrm{kJ\ mol^{-1}})$	$\Delta S_i^\ominus/(\mathrm{J\ mol^{-1}})$
0	0.000	19.923	1.466	−61.907
10	0.027	21.065	1.323	−66.215
20	0.058	22.378	1.407	−70.336
30	0.096	23.920	1.490	−75.228
40	0.141	25.803	1.611	−81.140
50	0.198	28.201	1.868	−88.322
60	0.270	31.227	2.306	−97.002
70	0.356	34.823	3.984	−104.441

4. Discussion

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

$$^{s}\delta\Delta H = (\Delta H_i^\ominus)_X - (\Delta H_i^\ominus)_{X=0} \tag{1}$$

The $^{s}\delta\Delta H$ values of the three nitrobenzoic acids are plotted against X_{DMF} in Fig. 1. Thermodynamic functions for the ionization of benzoic acid in water–DMF mixtures were obtained from the literature [5].

The $^{s}\delta\Delta H$ values increase monotonically with increasing mole fraction of DMF. This can be ascribed to the different solvation which the molecules and the ions of the three nitro isomers undergo in the mixtures. The desolvation of the anions plays

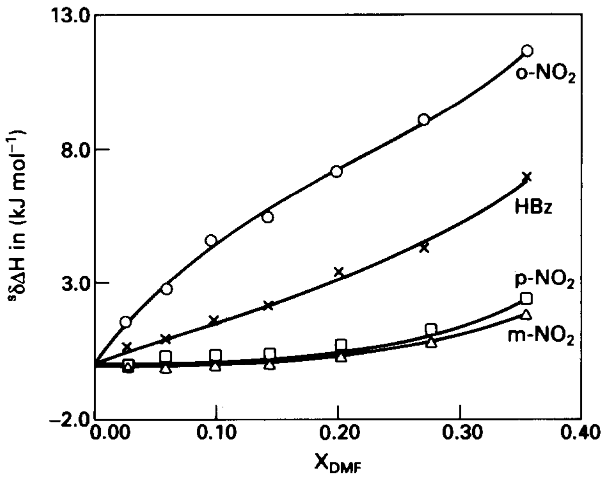

Fig. 1. $^{s}\delta\Delta H$ of the three nitrobenzoic acids vs. X_{DMF}.

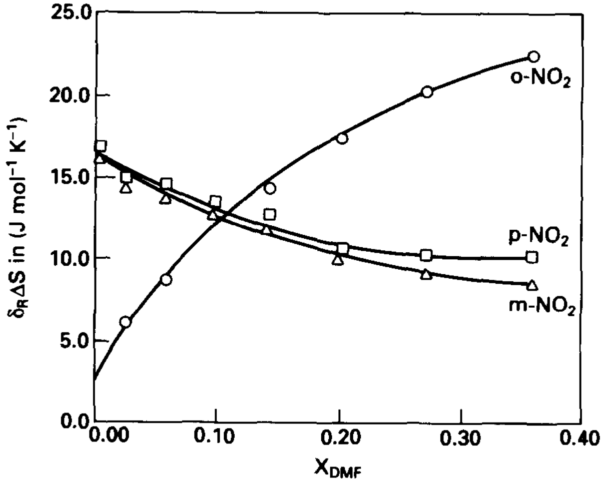

Fig. 2. $\delta_R \Delta S$ of the three nitrobenzoic acids vs. X_{DMF}.

a much more important role than that of undissociated molecules. DMF behaves towards water as a structure-breaker. With the increase in the DMF content, hydrogen bonds are formed between water and DMF molecules in the mixtures, and the number of H_2O molecules decreases. As a result, the anion is less solvated and an increasing trend is displayed.

The substituent effect may be written as

$$\delta_R \Delta S = \Delta S^{\ominus}(\text{RphCOOH}) - \Delta S^{\ominus}(\text{phCOOH}) \tag{2}$$

where $\delta_R \Delta S$ represents the substituent effect, and $\Delta S^{\ominus}$(RphCOOH) and $\Delta S^{\ominus}$(phCOOH) are the entropy values of substituted benzoic acid and benzoic acid in water–DMF mixtures respectively. Fig. 2 shows the relation between the $\delta_R \Delta S$ values of the three nitro isomers and X_{DMF} in the mixtures.

For *m*- and *p*-nitrobenzoic acid, the $\delta_R \Delta S$ values decrease with increasing DMF content. For *m*-NO_2, this trend can be related to the strong electron inductive effect of $-NO_2$ on the aromatic ring, which causes the diminished solvation of the anions. With an increase in the DMF content, the mixtures displayed a disordered structure, and the effect of substituent groups on solvating power is not so strong as that in water. For *p*-NO_2, an electron-accepting resonance effect also exists, so that for all mole fractions, $\delta_R \Delta S(p\text{-}NO_2) > \delta_R \Delta S(m\text{-}NO_2)$. For *o*-nitrobenzoic acid, the opposite result is obtained: the $\delta_R \Delta S$ values increase monotonically from a very low initial value in pure water which is mainly attributed to the ortho effect. No resonance interaction is to be expected in water for the anions because in the *o*-nitro compound the $-NO_2$ and $-COO^-$ groups are not in the same plane as the benzene ring [6]. Therefore, for *o*-nitro anions, the density of the negative charge is much higher than that for the other nitrobenzoic acids, which allows much stronger interactions between $-COO^-$ and H_2O molecules. This explains the very low value of $\delta_R \Delta S(o\text{-}NO_2)$ in pure water and its exceptional behaviour in the mixtures.

Many factors influence the behaviour of the anions in mixed solvents; further investigation is desirable.

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