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Note

Ionization thermodynamics of methylbenzoic acids in water–DMF mixtures

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Abstract

The ionization enthalpies of *p*-, *m*- and *o*-methylbenzoic 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; Methylbenzoic acid

1. Introduction

Substituted benzoic acids have been researched extensively. A thermodynamic study of the dissociation of *p*-, *m*- and *o*-nitrobenzoic acid in water–DMF mixtures as a function of the mole fraction has been performed in our laboratory [1] and has given further insight into the solvent effect on the different substituted acids.

2. Experimental

The heats of ionization of the three methylbenzoic acids (*p*-, *m*-, *o*-) were calculated indirectly from the heats of libration of these acids from the corresponding sodium salt

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solutions measured with an LKB 2277 Bioactivity Monitor at 298.15 K. The details of the experiment have been described previously [2].

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 mass 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 very dilute salt concentrations for each acid were carried out and extrapolated graphically to obtain the enthalpies of ionization at infinite dilution ($\Delta_i H^\circ$) for the acids concerned.

3. Results and discussion

Tables 1–3 show the enthalpy values of the three methylbenzoic acids in eight water–DMF mixtures at infinite dilution, and the corresponding calculated Gibbs free energies and entropies of ionization.

For the sake of comparison, it is convenient to express the effect of solvent on the ionization enthalpy values as the difference between the values obtained in the mixed

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

W_{DMF}	X_{DMF}	$\Delta_i G^\circ$/(kJ mol^{-1})	$\Delta_i H^\circ$/(kJ mol^{-1})	$\Delta_i S^\circ$/(J mol^{-1} K^{-1})
0	0.000	24.890	0.400	−82.140
10	0.027	26.146	1.205	−83.652
20	0.058	27.635	1.641	−87.168
30	0.096	29.400	2.213	−91.185
40	0.141	31.512	3.007	−95.607
50	0.198	34.195	4.328	−100.175
60	0.270	37.620	5.739	−106.931
70	0.356	41.617	7.812	−113.381

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

W_{DMF}	X_{DMF}	$\Delta_i G^\circ$/(kJ mol^{-1})	$\Delta_i H^\circ$/(kJ mol^{-1})	$\Delta_i S^\circ$/(J mol^{-1} K^{-1})
0	0.000	22.321	−5.627	−93.738
10	0.027	23.577	−3.051	−89.311
20	0.058	25.061	−0.922	−87.150
30	0.096	26.831	0.945	−86.823
40	0.141	29.000	2.984	−87.259
50	0.198	31.626	4.986	−89.352
60	0.270	35.052	6.983	−94.142
70	0.356	39.105	10.138	−97.155

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

W_{DMF}	X_{DMF}	$\Delta_i G^\circ$/(kJ mol^{-1})	$\Delta_i H^\circ$/(kJ mol^{-1})	$\Delta_i S^\circ$/(J mol^{-1} K^{-1})
0	0.000	24.376	0.180	−81.154
10	0.027	25.632	0.450	−84.462
20	0.058	27.059	1.076	−87.149
30	0.096	28.772	1.794	−90.484
40	0.141	30.884	2.764	−94.316
50	0.198	33.510	3.632	−100.212
60	0.270	36.878	5.272	−106.008
70	0.356	40.874	7.487	−111.982

solvent of X mole fraction and in pure water, so that

$$^{s}\delta\Delta H = (\Delta_i H^\circ)_X - (\Delta_i H^\circ)_{X=0}$$

The $^{s}\delta\Delta H$ values of the three methylbenzoic acids are plotted against X_{DMF} in Fig. 1. Thermodynamic functions of ionization of benzoic acid in water–DMF mixtures were obtained from the literature [3].

As with the nitrobenzoic acids previously reported [1], the $^{s}\delta\Delta H$ values of the methlybenzoic acids increase monotonically with increasing mole fraction of DMF in water–DMF mixtures. This can be ascribed to the decrease in the solvation of dissociated anions of the three methyl isomers in the water–DMF mixtures compared with that in the aqueous solution. The desolvation of the anions plays a much more important role than that of undissociated molecules. DMF behaves towards water as

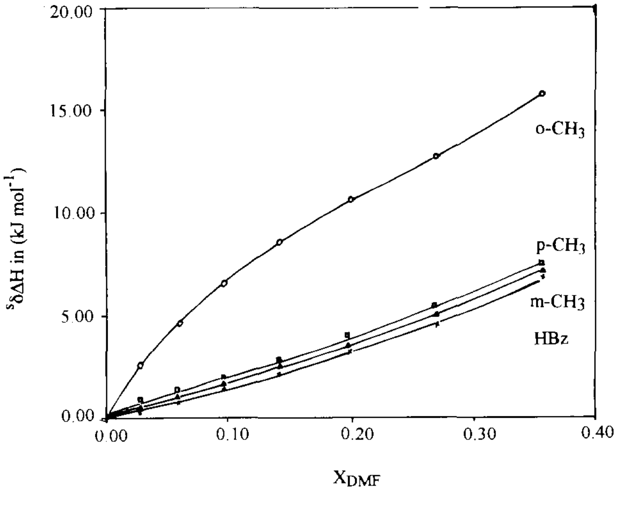

Fig. 1. $^{s}\delta\Delta H$ of the three methylbenzoic acids vs. X_{DMF}.

a structure-breaker. With the increase in the DMF content, strong hydrogen bonds are formed between water and DMF molecules in the mixtures, and the number of water molecules decreases. As a result, this stabilizes the charged particles ($RphCOO^-$). When the substituted acid ion ($RphCOO^-$) transfers from water to water–DMF mixtures, the anion is less solvated and so an increasing trend is displayed.

The substituent effect may be written as

$$\delta_R \Delta S = \Delta S^\circ(\text{RphCOOH})\text{-}\Delta S^\circ(\text{phCOOH})$$

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

For *m*- and *p*-methylbenzoic acid, the $\Delta\delta_R \Delta S$ values increase slightly with increasing DMF content. For *m*-CH_3, this trend can be related to the electron-donating effect of $-CH_3$ on the aromatic ring, which enhances the solvation of the anions. With an increase in the DMF content, the mixtures display a disordered structure, and the effect of substituent groups on solvating power is stronger than that in water. For *p*-CH_3, a weak electron-accepting resonance effect also exists, so that for all mole fractions: $\delta_R \Delta S(p\text{-}CH_3) < \delta_R \Delta S(m\text{-}CH_3)$. For *o*-methylbenzoic acid, a completely different result is obtained: the $\delta_R \Delta S$ values increase monotonically from a very low initial value in pure water. This is mainly attributed to the ortho-effect, which has attracted much attention [4, 5].

The anions of the *o*-methyl compound are much more solvated in pure water than in water–DMF mixtures owing to the steric effect, which is similar to the result obtained from *o*-nitrobenzoic acid [1]. For *m*- and *p*- nitrobenzoic acid, however, the $\delta_R \Delta S$ values decrease with increasing DMF content, and are completely different from the

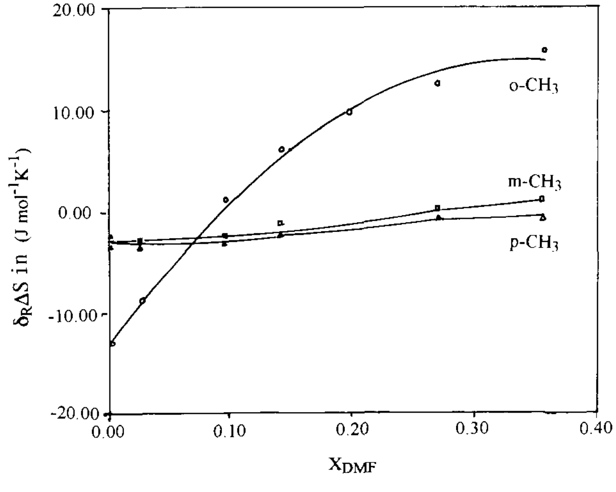

Fig. 2. $\delta_R \Delta S$ of the three methylbenzoic acids vs. X_{DMF}.

methylbenzoic acid results obtained in this work. The difference can be related to the strong electron-inductive effect of $-NO_2$ on the aromatic ring, which causes the diminished solvation of the anions. For p-NO_2, an electron-accepting resonance effect also exists, so that for all mole fractions: $\delta_R \Delta S(p\text{-}NO_2) > \delta_R \Delta S(m\text{-}NO_2)$. This result is the opposite to that displayed in the methylbenzoic acids, which is $\delta_R \Delta S(p\text{-}CH_3) < \delta_R S(m\text{-}CH_3)$.

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