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Thermodynamics of ionization processes for fluoro-substituted benzoic acids in water–dimethylformamide mixtures at 298.15 K

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Abstract

The ionization enthalpies, ΔH^0, of benzoic acid, *o*- and *p*-fluorobenzoic acids were measured calorimetrically at 298.15 K in water–dimethylformamide (DMF) mixtures ranging from pure water up to 0.7 weight-fraction DMF. The ionization Gibbs energies, ΔG^0, of the acids in the same solutions were measured by the conductance method. The corresponding entropies, ΔS^0, of ionization were calculated. The effect of solvent and substituent on the thermodynamic properties of ionization were considered. © 1998 Elsevier Science B.V.

Keywords: Benzoic acid; *o*-Fluorobenzoic acid, *p*-fluorobenzoic acid; Ionization enthalpy; Ionization entropy; Ionization Gibbs energy

1. Introduction

The ionization of chlorobenzoic acids and nitrobenzoic acids in water–EtOH and in water–dimethylformamide (DMF) mixtures have been studied by our laboratory [1–3]. A knowledge of ΔH^0, ΔG^0 and ΔS^0 values is important for the understanding of acid strength trends in various solvents.

Dimethylformamide has been extensively used as a solvent in various fields of chemistry. The moderately high dielectric constant and aprotic nature make it particularly useful for acid–base studies.

In the present work, the ionization behaviour of *o*- and *p*-fluorobenzoic acid in water–DMF mixtures has been examined.

2. Experimental and Procedure

The calorimetric measurements were performed using an LKB 2277 BioActivity monitor. All the measurements were carried out at 25±0.0005°C.

The principle of the measurement was shown in Fig. 1. Two reagents A and B were pumped into the calorimeter by two wriggle pumps. A and B were mixed and reacted at C rapidly, then flowed out at point F. During the flowing process, the thermal power of the reaction was inspected at points D and E, and was amplified, displayed and recorded.

DMF (AR grade) was purified according to the procedure of Ritchie and Megerle [4]. Water–DMF mixtures were prepared by weighing purified DMF and CO_2-free, double-distilled water.

The weight fraction of DMF in these mixtures ranged from 0.1 to 0.7. Aqueous solutions of 0.1 M

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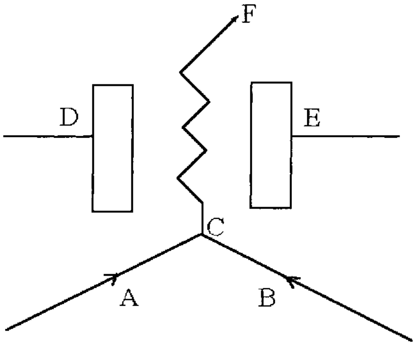


Fig. 1. The principle of measurement.

$HClO_4$ and 0.1 M NaOH were prepared from standard solutions and their concentrations were checked by acid–base titrations, phenolphthalein was chosen as acid–base indicator. *o*-Fluorobenzoic acid (AR grade) and *p*-fluorobenzoic acid (laboratory reagent) were stored in a vacuum dryer, the acid purities 99.5% minimum. The acids underwent no further purification.

The enthalpies of ionization of the fluorobenzoic acids were calculated indirectly from the heats of liberation of these acids from the corresponding sodium salt solutions. The fluorobenzoic sodium salt solutions were prepared by adding NaOH aqueous solutions of known molarity to fluorobenzoic acids dissolved in the mixed solvent. As a result, 100 g of water–DMF solution at W_{DMF} weight fraction was obtained. The concentration of the sodium salt was always in the 2×10^{-4}–1.5×10^{-3} mol/100 g range. A certain amount of acid (ca. 4–5% of the original content) was not converted into the salt and remained as free acid to avoid the presence of free alkali.

The $HClO_4$ solution in water–DMF mixture was prepared by adding $HClO_4$ aqueous solution of known molarity to mixed solvent. As a result, $HClO_4$ solution in water–DMF mixture at W_{DMF} weight fraction was obtained. The concentration of the $HClO_4$ solution was ca. 1.8×10^{-3} mol/100 g.

The ionization process of HB_ZO_S (where subscript s indicates the substituted acids) in various water–DMF mixtures of *W* weight fraction can be represented as

$$(HB_ZO_S)_W \rightarrow (H^+)_W + (B_ZO_S^-)_W. \quad (1)$$

The molar enthalpy of process (1) is the molar enthalpy ΔH^0 of ionization of HB_ZO_S in mixed solvent of *W* weight fraction. ΔH^0 was obtained by the following experimental measurements:

(1) The molar enthalpy of reaction ΔH_1 of the sodium salt NaB_ZO_S dissolved in the mixed solvent of *W* weight fraction, with $HClO_4$ also dissolved in *W* weight fraction

$$(Na^+)_W + (B_ZO_S^-)_W + (H^+)_W + (ClO_4^-)_W \rightarrow (HB_ZO_S)_W + (Na^+)_W + (ClO_4^-)_W. \quad (2)$$

During the reaction, ca. 10% $HClO_4$ was excess to avoid the dissociation of HB_ZO_S.

(2) The molar enthalpy of dilution of NaB_ZO_S and $HClO_4$ in the reaction process, the values are Qs and Qa for $HClO_4$ and NaB_ZO_S, respectively.

The molar ionization enthalpy of HB_ZO_S is:

$$\Delta H^0 = -(\Delta H_1 - \mathrm{Qs} - \mathrm{Qa}). \quad (3)$$

In the experiment, NaB_ZO_S and $HClO_4$ ionized thoroughly in water–DMF mixtures and the mixing heats between ions were negligible. The postulate is reasonable in dilute solution.

Duplicate runs at five different salt concentrations for each acid were carried out and extrapolated graphically in order to obtain the enthalpies of ionization at infinite dilution for the acids concerned, the results varied within ±1%.

The dissociation constants of *o*- and *p*-fluorobenzoic acids were measured by conductance method as described in literature [5]. The temperature of water baths was controlled at 25±0.01°C.

3. Results

Table 1 shows the enthalpies of ionization of benzoic acid, *o*- and *p*-fluorobenzoic acids in water–DMF mixtures at infinite dilution. Tables 2 and 3 show the corresponding Gibbs energies and entropies of ionization of the three acids, respectively.

In order to illustrate the effect of solvent on the enthalpy, Gibbs energy and entropy of ionization, it is convenient to express the ionization enthalpy as difference between the values obtained in the mixed solvent of *W* weight fraction and in pure water, it gives

$$\delta\Delta H^0 = (\Delta H^0)_W - (\Delta H^0)_{W=0} \quad (4)$$

$\delta\Delta G^0$ and $T\delta\Delta S^0$ can be defined in a similar way.

Table 1
Molar enthalpies of ionization ΔH^0 (kJ mol^{-1}) of benzoic acid, *o*- and *p*-fluorobenzoic acids in water–DMF mixtures of various weight fractions at 298.15 K

W_{DMF}	H [a]	*o*-F [b]	*p*-F [c]
0	0.418±0.021	−4.414±0.013	1.134±0.017
0.1	0.797±0.003	−2.373±0.010	1.465±0.008
0.2	1.217±0.010	−1.808±0.008	1.966±0.003
0.3	1.921±0.015	−1.107±0.001	2.371±0.006
0.4	2.548±0.001	−0.572±0.001	3.102±0.012
0.5	3.771±0.001	0.499±0.003	3.403±0.026
0.6	4.826±0.041	1.907±0.001	4.282±0.004
0.7	7.397±0.033	4.025±0.016	6.499±0.007

[a] Benzoic acid.
[b] *o*-Fluorobenzoic acids.
[c] *p*-Fluorobenzoic acids.

These three δ-values are relative to the transfer of ionization process. The three δ-values of benzoic acid, *o*- and *p*-fluorobenzoic acids are plotted against W_{DMF} in Figs. 2–4.

In order to illustrate the effect of substituent on the enthalpy, Gibbs energy and entropy of ionization, a difference between the corresponding values of fluoro-substituted benzoic acid and benzoic acid were obtained as:

$$\delta_S\Delta H^0 = (\Delta H^0_{\text{fluorobenzoic acid}})_W - (\Delta H^0_{\text{benzoic acid}})_W \tag{5}$$

$\delta_S\Delta G^0$ and $T\delta_S\Delta S^0$ can be defined similarly. The three δ_S-values of *o*- and *p*-fluorobenzoic acids are plotted against W_{DMF} in Fig. 5.

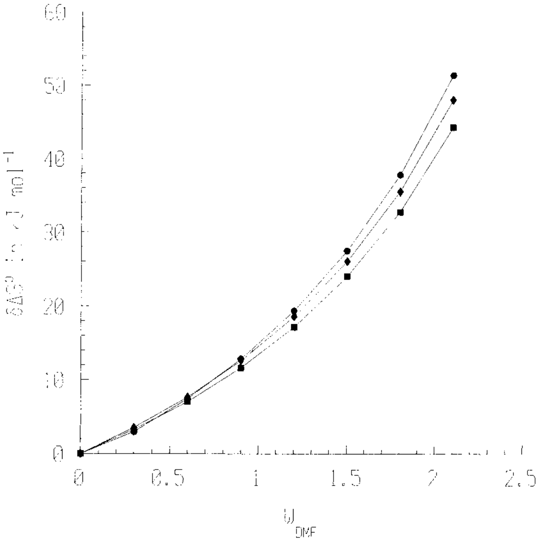


Fig. 2. Gibbs energies of ionization for the transfer of the three acids from water to water–DMF mixtures, as a function of the weight fraction at 298.15 K. ●, benzoic acid; ◆, *o*-fluorobenzoic acid; ■, *p*-fluorobenzoic acid.

4. Discussion

The $\delta\Delta H^0$ term, as shown in Fig. 3, is unfavourable to process (1) in the complete weight fraction range.

Table 2
Molar Gibbs energies of ionization ΔG^0 (kJ mol^{-1}) of benzoic acid, *o*- and *p*-fluorobenzoic acids in water–DMF mixtures of various weight fractions at 298.15 K

W_{DMF}	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7
H	23.890	24.872	26.368	28.161	30.340	33.046	36.497	41.047
o-F	18.664	19.836	21.210	22.856	24.858	27.342	30.510	34.689
p-F	23.630	24.710	25.977	27.495	29.340	31.630	34.552	38.405

Table 3
Molar entropies of ionization ΔS^0 (J mol^{-1} K^{-1}) of benzoic acid, *o*- and *p*-fluorobenzoic acids in water–DMF mixtures of various weight fractions at 298.15 K

W_{DMF}	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7
H	−78.72	−80.75	−84.36	−88.01	−93.21	−98.19	−106.23	−112.86
o-F	−77.40	−74.49	−77.20	−80.37	−85.29	−90.03	−95.93	−102.85
p-F	−75.45	−77.96	−80.53	−84.27	−88.00	−94.67	−101.53	−107.01

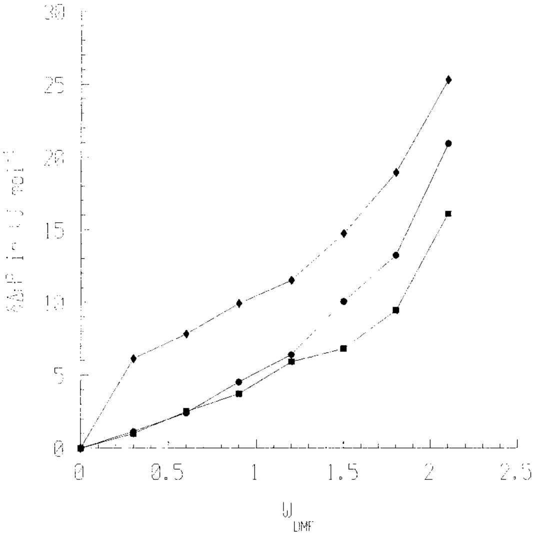


Fig. 3. Enthalpies of ionization for the transfer of the three acids from water to water–DMF mixtures, as a function of the weight fraction at 298.15 K. ●, benzoic acid; ◆, *o*-fluorobenzoic acid; ■, *p*-fluorobenzoic acid.

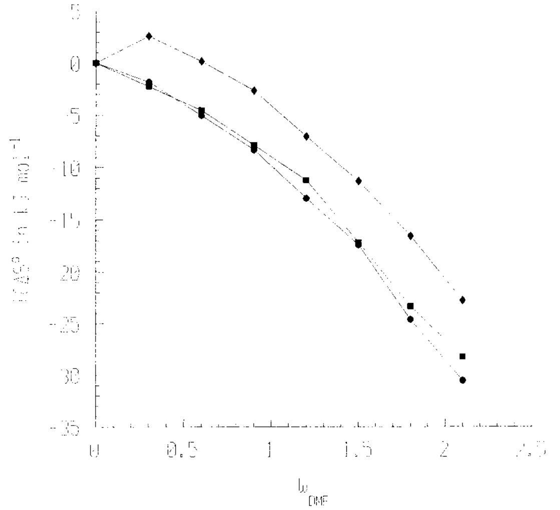


Fig. 4. Entropies of ionization for the transfer of the three acids from water to water–DMF mixtures, as a function of the weight fraction at 298.15 K. ●, benzoic acid; ◆, *o*-fluorobenzoic acid; ■, *p*-fluorobenzoic acid.

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

The $\delta\Delta H^0$ values for the transfer of the three acids from water to water–DMF mixtures are positive and

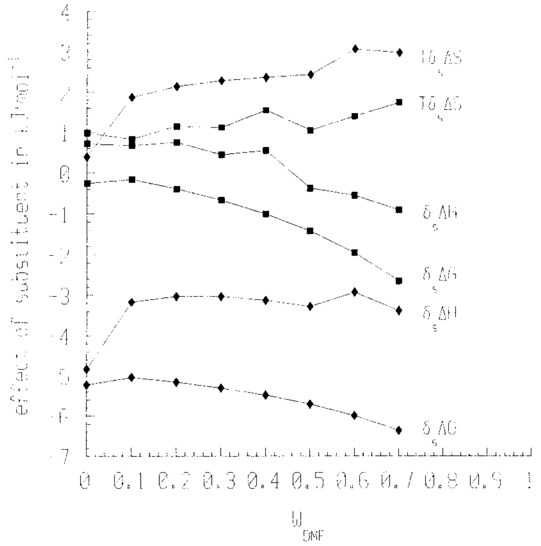
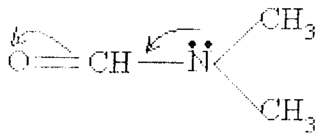


Fig. 5. The differences of ionization thermodynamic properties of the three acids from water to water–DMF enthalpy between fluorobenzoic acid and benzoic acid in water–DMF mixtures, as a function of the weight fraction at 298.15 K. ◆, *o*-fluorobenzoic acid; ■, *p*-fluorobenzoic acid.

increase with increasing DMF content. DMF molecules are the smallest amide molecules without intermolecular hydrogen bonding, the structure of DMF is:



The side with positive charge in the molecule is surrounded by two methyl groups, the side with negative charge is exposed to the outside. So, the addition of DMF into mixed solvent is unfavourable for the solvation of the $B_ZO_S^-$ anion; on the contrary, it is favourable for the solvation of undissociated molecule of HB_ZO_S. The desolvation of the anions plays a much more important role than that of undissociated molecules. As a result, an increasing $\delta\Delta H^0$ trend is displayed.

The order of ΔH^0 value of the three acids can be observed from Table 1. *o*-Fluorobenzoic acid is more exothermic than benzoic acid and *p*-fluorobenzoic acid in water–DMF mixtures. When $W_{DMF}\leq 0.4$, benzoic acid is less endothermic than *p*-fluorobenzoic acid; on the contrary, when $W_{DMF}>0.4$, benzoic acid is more endothermic than *p*-fluorobenzoic acid.

According to Hepler [6], the ionization enthalpy of acid can be divided into internal contribution and environmental contribution. The first term arises from difference in enthalpy within the acid molecule and its anion, expressed as ΔH_{int}. The second term is associated with solute–solvent interaction, expressed as ΔH_{env}.

For *o*-fluorobenzoic acid, because of steric hindrance [7], its anion exists as stereo configuration, i.e. –F, and $-COO^-$ are not in the same plane as the benzene ring [8], the density of the negative charge is higher than that for benzoic acid and *p*-fluorobenzoic acid, which allows much stronger interaction between $-COO^-$ and H_2O molecules. Therefore, for ΔH^0, *o*-fluorobenzoic acid is more exothermic than benzoic acid and *p*-fluorobenzoic acid. The solvation of *o*-fluorobenzoic anion becomes weaker progressively with increasing DMF content in water–DMF mixtures, the stereo configuration changes to plane configuration, the enthalpy of ionization of *o*-fluorobenzoic acid becomes less exothermic and more close to those of benzoic acid and *p*-fluorobenzoic acid.

Owing to the electron-attractive effect of the fluorine atom, the order of ΔH_{int} is: *p*-fluorobenzoic acid<benzoic acid; on the contrary, the order of ΔH_{env} is: *p*-fluorobenzoic acid>benzoic acid. From Table 1, the following order of ΔH is observed in aqueous solution: *p*-fluorobenzoic acid>benzoic acid. It shows that the difference of ΔH_{env} is larger than that of ΔH_{int} in aqueous solution. On the addition of DMF into water, the solvation of anion becomes weaker and the difference ΔH_{env} becomes smaller. Therefore when $W_{DMF}>0.4$, the order of ΔH is: *p*-fluorobenzoic acid> benzoic acid.

From the work of Strong et al. [9], the ionization enthalpies of some substituted benzoic acids in aqueous solution vary with temperature, the higher the temperature, the more exothermic the enthalpies. The heat capacity change for the ionization of acids can be expected to change with composition of the solvent, the order of ionization enthalpies may be different at another temperature. The temperature effect on ionization process in mixed solvents needs further study.

The $\delta\Delta G^0$ term, as shown in Fig. 2, is unfavourable to the ionization of benzoic acid and fluorobenzoic acid. This phenomenon can be explained by the dielectric constants of the mixed solvents.

The $T\delta\Delta S^0$ term, as shown in Fig. 4, is unfavourable to the ionization of benzoic acid and *p*-fluorobenzoic acid also. Compared with benzoic acid or *p*-fluorobenzoic acid. When $W_{DMF}<0.2$, *o*-fluorobenzoic acid shows speciality due to its steric hindrance; however, when $W_{DMF}>0.2$, the property disappears.

The curves of Fig. 5 give the effect of substituent on the ionization thermodynamic properties in water–DMF mixtures. From Gibbs energy point of view, the strength order of the acids is: *o*-fluoro>*p*-fluoro> benzoic acid.

From enthalpy point of view, the following phenomena can be observed: (1) the substituent effect of *o*- and *p*-fluoro on substituted benzoic acid is obviously different. For *o*-fluorobenzoic acid, the $\delta_S\Delta H^0$ term is exothermic in the complete weight-fraction range, whereas for *p*-fluorobenzoic acid, the $\delta_S\Delta H^0$ term varies from endothermic to exothermic. (2) For *o*-fluorobenzoic acid, the $\delta_S\Delta H^0$ term is more exothermic in aqueous solution than in mixed solvents, and keeps almost a constant value in mixed solvents.

From entropy point of view, the effect of solvent on the ionization entropy is stronger for the *o*-substituent than that for the *p*-substituent.

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