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Thermochimica Acta 317 (1998) 201–203

thermochimica acta

Thermodynamics of ionization of *o*-fluoro and *o*-chloro benzoic acids in water–ethanol mixtures at 298.15 K

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Received 30 October 1997; received in revised form 3 April 1998; accepted 6 May 1998

Abstract

The ionization enthalpies of ΔH° of *o*-fluoro and *o*-chloro benzoic acids were measured by LKB 2277 BioActivity Monitor at 298.15 K in water–ethanol mixtures from pure water up to 0.8 weight fraction ethanol. The ionization-free enthalpies ΔG° of the two acids in the same mixtures were obtained from published literature. The corresponding entropies ΔS° of ionization were calculated from the values of ΔH° and ΔG°. © 1998 Elsevier Science B.V.

Keywords: Ionization enthalpy; Ionization entropy; Benzoic acid; *o*-Fluorobenzoic acid; *o*-Chlorobenzoic acid

1. Introduction

The study of ionization thermodynamic process for substituted benzoic acids is helpful to our understanding of substituent and solvent effects. For *o*-substituents, due to their steric hindrance [1,2], the effects on the ionization of substituted benzoic acids are different from those of *meta*- and *para*-substituents. Water–ethanol mixtures have been extensively used as solvents in laboratory research and in chemical industry production.

In the present work, the ionization behaviour of *o*-fluoro and *o*-chloro benzoic acids in water–enthanol mixtures has been examined.

2. Experimental and procedure

The calorimetric apparatus is a LKB 2277 BioActivity monitor. Ethanol (G.R.) was purified in the usual way. Water–ethanol mixtures were prepared by weight from CO_2-free twice-distilled water and purified ethanol. The weight fraction of ethanol in the mixtures ranges from 0.1 to 0.8. Aqueous solutions of 0.1 N HNO_3 and NaOH were prepared from standard solutions. *o*-fluoro and *o*-chloro benzoic acids were stored in a vacuum dryer, and underwent no further purification. The procedure of the measurement has been given in our earlier work [3]. All measurements were carried out at 298.15 K.

3. Results and discussion

Table 1 shows the enthalpies of ionization of benzoic acid, *o*-fluoro and *o*-chloro benzoic acids in

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PII S0040-6031(98)00375-X

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

W_{EtOH}	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
H	0.418	−0.809	−1.243	1.882	4.597	4.455	2.978	0.187	−2.608
o-F	−4.414	−4.318	−3.993	−1.624	1.003	1.125	−0.373	−2.793	−5.214
o-Cl	−10.43	−10.02	−9.736	−5.111	−1.376	−1.112	−2.477	−5.024	−8.263

Note: H indicates benzoic acid, *o*-F and *o*-Cl indicate *o*-fluoro and *o*-chloro benzoic acids, respectively.

water–ethanol mixtures at 298.15 K, in which the ionization enthalpies of benzoic acid are obtained from the work of Zhang [4]. Tables 2 and 3 show the corresponding free enthalpies and entropies of ionization of the three acids respectively. The free enthalpies of ionization of the three acids are obtained from published literature [5].

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

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

The δ values are relative to the transfer of the ionization process. The δ values are plotted against W_{EtOH} in Fig. 1.

From the results in Table 1 and Fig. 1, it should be noted that the ionization enthalpy values of benzoic acid and *o*-fluoro and *o*-chloro benzoic acids show maxima at the weight fraction of ethanol around 0.4–0.5 in water–EtOH mixtures. The maxima is related to the properties of water–EtOH mixtures. Due to the hydrogen bond formed between the same kind of molecules and different kinds of molecules in water–ethanol mixtures, many thermodynamic and spectrum properties show extrema in low ethanol content [6].

In order to illustrate the effect of the substituent on the entropy of ionization, a difference between the corresponding values of *o*-halogenated benzoic acid and benzoic acid were obtained as:

$$\delta_S\Delta S^0 = (\Delta S^0_{\text{halobenzoic acid}})_W - (\Delta S^0_{\text{benzoic acid}})_W$$

The δ_S values of halobenzoic acid are plotted against W_{EtOH} in Fig. 2.

The results in Fig. 2 show that the influence of solvents on the substituent effects of *o*-fluorine and

Table 2
Molar-free enthalpies of ionization ΔG^0 (kJ mol^{-1}) of benzoic acid, *o*-fluoro and *o*-chloro benzoic acids in water–EtOH mixtures of various weight fractions at 298.15 K

W_{EtOH}	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
H	23.890	25.628	27.226	28.881	30.650	32.476	34.360	36.587	38.926
o-F	18.664	20.834	23.003	25.227	27.397	29.566	31.335	33.333	35.673
o-Cl	16.550	18.835	21.004	23.003	24.942	26.883	28.709	30.765	32.876

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

W_{EtOH}	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
H	−78.72	−88.67	−95.49	−90.56	−87.38	−93.98	−105.26	−122.09	−139.31
o-F	−77.40	−84.36	−90.55	−90.06	−88.53	−95.37	−106.35	−121.17	−137.14
o-Cl	−90.49	−96.77	−103.10	−94.29	−88.27	−93.90	−104.60	−120.04	−137.98

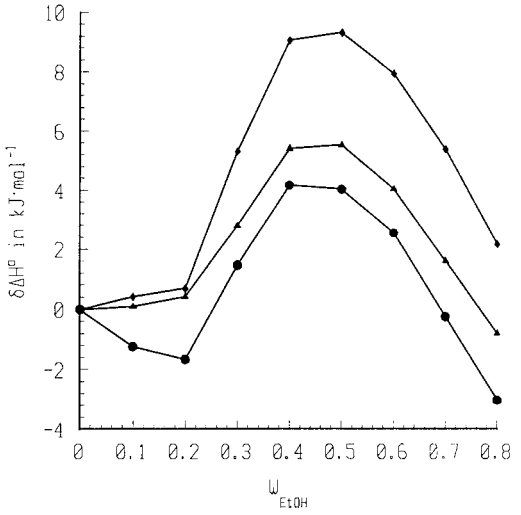

Fig. 1. Enthalpies of ionization for the transfer of the three acids from water to water–EtOH mixtures, as a function of the weight fraction at 298.15 K ●: benzoic acid; ▲: *o*-fluoro benzoic acid; ◆: *o*-chloro benzoic acid.

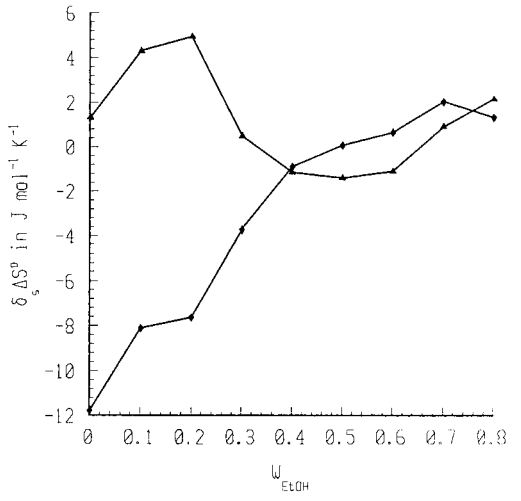

Fig. 2. Differences of ionization entropy between *o*-halogenated benzoic acid and benzoic acid in water–EtOH mixtures, as a function of the weight fraction at 298.15 K. ▲: *o*-fluoro benzoic acid; ◆: *o*-chloro benzoic acid.

o-chlorine atoms is different; this phenomenon is related to the size of an adjacent group. From the work of Charton [7], the steric effect is based on the Van der Waals radius of the adjacent group, the larger the size of the adjacent group, the stronger the steric effect.

Acknowledgements

The authors thank the National Committee of Science and Technology (China) for financial support.

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