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Ionization thermodynamics of methylbenzoic acids in EtOH–H_2O mixtures

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Abstract

Ionization enthalpies of *o*-, *m*- and *p*-methylbenzoic acids in ethanol–water mixtures have been determined. Combined with corresponding free energies, the ionization entropies have been calculated. The substituent and solvent effects on the ionization thermodynamics are discussed in terms of solute–solvent interactions and the structure of ethanol–water mixtures.

1. Introduction

The ionization thermodynamics of substituted organic acids in aqueous ethanol and DMF has been a subject of extensive research in our laboratory [1–7]. This work, and that for several substituted benzoic acids in DMSO–H_2O mixtures by Rodante et al. [8], have led to useful information on the acidity behavior of weak acids, solute–solvent interactions, and linear free-energy relations. As a part of our continuing research, the ionization thermodynamics of *o*-, *m*-, and *p*-methylbenzoic acids in EtOH–H_2O mixtures are reported in this paper.

2. Experimental

The calorimeter, LKB-2277 BioActivity Monitor, is used in the mode of mixing-flow at 298.15 K. The details of the determination of ionization enthalpies have been described previously [1–3].

The three isomers of methylbenzoic acid are all pure products from Fluka. The acids were recrystallized twice from EtOH–H_2O mixtures and their melting points checked before use. EtOH–H_2O mixed solvents were prepared volumetrically, ranging from 0–80%.

3. Results

The ionization enthalpies (ΔH_i^0) of the three isomers in various EtOH–H_2O mixtures are shown in Tables 1–3 together with corresponding free energies (ΔG_i^0) calculated from pK_α values and entropies ($T\Delta S_i^0$) reported in the literature [9].

4. Discussion

Solvent effect on ionization can be defined as the enthalpic or entropic difference between the value obtained in the mixed solvent of x mole fraction and that in pure water.

$$\delta_s \Delta H_i^0 = (\Delta H_i^0)_x - (\Delta H_i^0)_w \quad (1)$$

$$T\delta_s \Delta S_i^0 = (T\Delta S_i^0)_x - (T\Delta S_i^0)_w \quad (2)$$

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Table 1
Thermodynamic functions of ionization of *o*-methylbenzoic acids in EtOH–H_2O mixtures at 298.15 K

v%	x_{EtOH}	$\varepsilon^{-1}\times10^{-2}$ [10]	ΔG_i^0/(kJ mol^{-1})	ΔH_i^0/(kJ mol^{-1})	$T\Delta S_i^0$/(kJ mol^{-1})
0	0.000	1.27	22.32	−5.86±0.00	−28.18
10	0.033	1.35	23.74	−6.26±0.05	−30.00
20	0.072	1.42	25.40	−5.65±0.06	−31.05
30	0.117	1.53	27.40	−2.35±0.07	−29.75
40	0.170	1.71	29.57	2.63±0.06	−26.94
50	0.236	1.90	31.39	4.84±0.06	−26.55
60	0.316	2.14	33.56	3.79±0.08	−29.77
70	0.418	2.44	35.44	1.50±0.15	−33.94
80	0.552	2.87	38.24	−1.85±0.08	−40.09

Table 2
Thermodynamic functions of ionization of *o*-methylbenzoic acids in EtOH–H_2O mixtures at 298.15 K

v%	x_{EtOH}	$\varepsilon^{-1}\times10^{-2}$ [10]	ΔG_i^0/(kJ mol^{-1})	ΔH_i^0/(kJ mol^{-1})	$T\Delta S_i^0$/(kJ mol^{-1})
0	0.000	1.27	24.37	0.18±0.05	−24.19
10	0.033	1.35	25.40	−0.60±0.04	−26.00
20	0.072	1.42	26.83	−0.80±0.04	−27.63
30	0.117	1.53	24.82	1.08±0.05	−27.34
40	0.170	1.71	30.36	4.46±0.10	−25.90
50	0.236	1.90	32.08	5.48±0.10	−26.60
60	0.316	2.14	34.13	4.30±0.15	−29.83
70	0.418	2.44	35.96	1.93±0.04	−34.03
80	0.552	2.87	38.53	−1.38±0.15	−39.91

Table 3
Thermodynamic functions of ionization of *o*-methylbenzoic acids in EtOH–H_2O mixtures at 298.15 K

v%	x_{EtOH}	$\varepsilon^{-1}\times10^{-2}$ [10]	ΔG_i^0/(kJ mol^{-1})	ΔH_i^0/(kJ mol^{-1})	$T\Delta S_i^0$/(kJ mol^{-1})
0	0.000	1.27	24.94	0.40±0.06	−24.54
10	0.033	1.35	26.03	−0.30±0.10	−26.44
20	0.072	1.42	27.40	−0.17±0.04	−27.57
30	0.117	1.53	29.00	−1.85±0.05	−27.15
40	0.170	1.71	30.82	5.03±0.05	−25.79
50	0.236	1.90	32.53	5.70±0.08	−26.83
60	0.316	2.14	34.65	4.33±0.06	−30.32
70	0.418	2.44	36.64	2.02±0.07	−34.62
80	0.552	2.87	39.44	−1.28±0.10	−40.72

The values of $\Delta_s\Delta H_i^0$ and $T\delta_s\Delta S_i^0$ for the three isomers of methylbenzoic acids are plotted against x_{EtOH} in Fig. 1.

As can be seen from Tables 1–3 and Fig. 1, the values of ΔG_i^0 increase monotonically with increasing mole fraction of EtOH, but both $\delta_s\Delta H_i^0$ and $T\delta_s\Delta S_i^0$ decrease, increase, and then decrease with increasing x_{EtOH}. The curves have a minimum around 0.1 mol fraction of EtOH and a maximum around 0.2 mol fraction of EtOH. Compensation between the enthalpic and entropic effects results in the monotonic variation of ΔG_i^0 with solvent composition.

Small amounts of aliphatic alcohols strengthen the three-dimensional structure of liquid water. In terms of Frank and Wen's 'flickering clusters' [11], the average

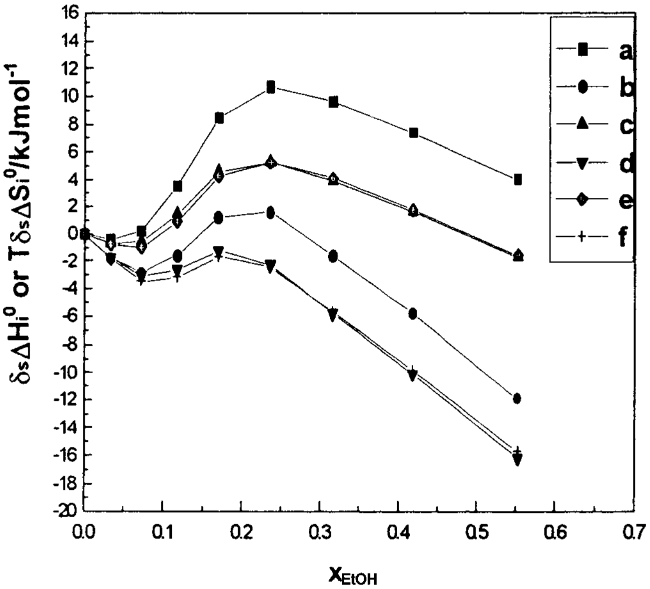

Fig. 1. Transfer enthalpy and entropy for ionization of *o*-, *m*-, *p*-methylbenzoic acids at 298.15 K. (a) $\delta_s\Delta H_i^0$; (ortho-), (b) $T\delta_s\Delta S_i^0$ (ortho-), (c) $\delta_s\Delta H_i^0$ (para-), (d) $T\delta_s\Delta S_i^0$ (para-), (e) $\delta_s\Delta H_i^0$ (meta-), and (f) $T\delta_s\Delta S_i^0$ (meta-).

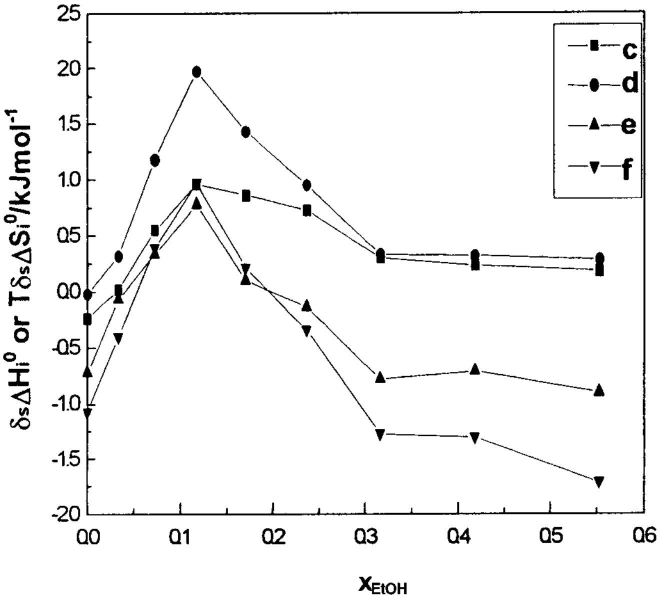

Fig. 2. The variations of $\delta_R\Delta H_i^0$ and $T\delta_R\Delta S_i^0$ with x_{EtOH} for *m*- and *p*-methylbenzoic acids at 298.15 K. (c) $\delta_R\Delta H_i^0$ (meta-), (d) $\delta_R\Delta H_i^0$ (para-), (e) $T\delta_R\Delta S_i^0$ (meta-), and (f) $T\delta_R\Delta S_i^0$ (para-).

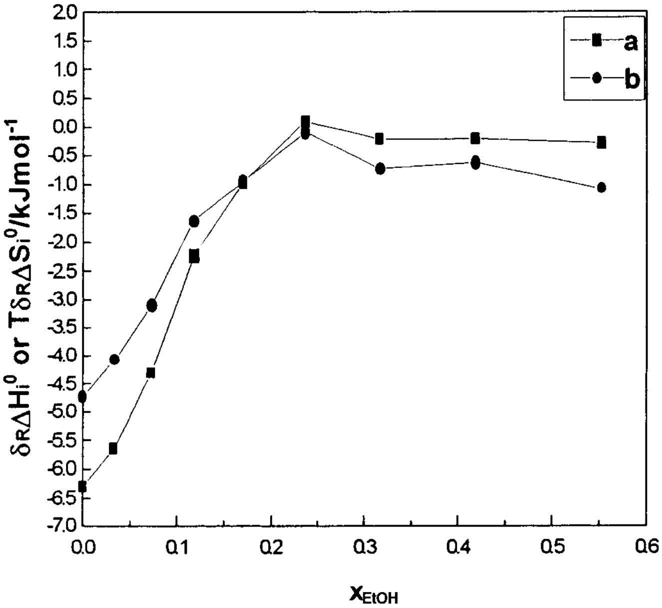

Fig. 3. The variations of $\delta_R\Delta H_i^0$ and $T\delta_R\Delta S_i^0$ with x_{EtOH} for *o*-methylbenzoic acid at 298.15 K. (a) $\delta_R\Delta H_i^0$ (ortho-), and (b) $T\delta_R\Delta S_i^0$ (ortho-).

lifetime of ice-like clusters is extended or, in other words, the equilibrium, 'iceberg'↔monomeric water, is shifted to the left in dilute alcohol–water mixtures compared with pure water.

The substituent effect can be expressed as

$$\delta_R\Delta H_i^0 = \Delta H_i^0(R\phi\mathrm{COOH}) - \Delta H_i^0(\phi\mathrm{COOH}) \tag{3}$$

$$T\delta_R\Delta S_i^0 = T\Delta S_i^0(R\phi\mathrm{COOH}) - \Delta S_i^0(\phi\mathrm{COOH}) \tag{4}$$

in which R represents a substituent at the various positions on the aromatic ring. Since the corresponding thermodynamic data for ionization of benzoic acid, have been reported by previously [7,12], the values of $\delta_R\Delta H_i^0$ and $T\delta_R\Delta S_i^0$ were calculated and plotted against x_{EtOH} in Figs. 2 and 3.$\delta_R\Delta H_i^0$ and $T\delta_R\Delta S_i^0$ are evaluated for the proton exchange reaction:

$$\mathrm{R}\phi\mathrm{COOH} + \phi\mathrm{COO}^- \Leftrightarrow \mathrm{R}\phi\mathrm{COO}^- + \phi\mathrm{COOH} \tag{5}$$

In view of the symmetry of reaction (5), the internal contribution to $T\delta_R\Delta S_i^0$ is nearly zero [13], $T\delta_R\Delta S_i^0$ is therefore considered to result from solute–solvent interactions. Thus, the analysis of $T\delta_R\Delta S_i^0$ should be more rewarding because entropy rather than enthalpy change is usually a better indicator of structural effects.

Each species in reaction (5) includes two different hydration centers, the hydrophilic center (COOH or $\mathrm{COO^-}$) and the hydrophobic center (ϕ or Rϕ).

When *m*-, and *p*-methyl groups, well known for their electron-repelling effect, transfer from neutral molecule to anion, they lead to a more concentrated negative charge density and enhanced solvation of the anion. This decreases the entropy of the system. Therefore, the values of the entropy change for reaction (5) in aqueous solution are negative (Fig. 2). With increasing content of EtOH in the mixtures, $T\delta_R\Delta S_i^0$ passes through a maximum around 0.1 mol fraction of EtOH (Fig. 2). Beyond this point, the values of $T\delta_R\Delta S_i^0$ decrease gradually. In the alcohol-rich region, $T\delta_R\Delta S_i^0$ varies only slightly with the composition of the solvent. Although the maximum must be related to the enhanced structure in EtOH–H_2O mixtures, an explanation for the phenomenon would require more information about solute–solvent interactions.

The behavior of *o*–methylbenzoic acid differs in the water-rich region (Fig. 3). This is ascribable to the steric effect of the ortho-substituent.

In the alcohol-rich region ($x_{\mathrm{EtOH}}>0.3$), differences among the three isomers are minimal because of the breakdown of ice-like structures and microheterogeneity.

By separating substituent effects into enthalpic and entropic contributions, it is possible to study the behavior of the isomers by means of the isomers from the effects of the medium, both on the reaction and the substituent constants (ρ, σ). In this way, the steric effect of the ortho-derivative can be stressed. Related studies can be found in elsewhere [7,14].

Acknowledgements

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References

[1] Xin Zhang, Ruisen Lin, Hanxing Zong, Wenshing Yen, Acta Chimica Sinica 48 (1990) 28.

[2] Xin Zhang, Ruisen Lin, Wenshing Yen, Acta Chimica Sinica 48 (1990) 295.

[3] Ruiding Hu, Wenshing Yen, Ruisen Lin, Qingsen Yu, Thermochim. Acta 183 (1991) 65.

[4] Jianhua Hu, Ping Zhuang, Rusen Lin, Thermochim. Acta 246 (1994) 243.

[5] Jianhua Hu, Ping Zhuang, Rusen Lin, Yongshu Xie, Thermochim. Acta 262 (1995) 227.

[6] Yanqing Nan, Qingsen Yu, Hanxing Zong, Ruisen Lin, Acta Physico-Chimica Sinica 11 (1995) 92.

[7] Yanqing Nan, Ruisen Lin, Qingsen Yu, Acta Chimica Sinica 55 (1997) 755.

[8] F. Rodante, G. Pistoia, Thermochim. Acta 83 (1985) 213.

[9] M.R. Thuaire, C.R. Acad. Sci. Paris, Ser. C 267 (1968) 993.

[10] P.K. Biswas, S.C. Lahiri, B.P. Dey, Bull. Chem. Soc. Jpn. 66 (1993) 2785.

[11] H.S. Frank, W.Y. Wen, Discuss Faraday Soc. 24 (1957) 133.

[12] Xin Zhang, Ionization thermodynamics of mono-substituted benzoic acids in H_2O–EtOH mixtures, Ph.D. Dissertation, Zhejiang University, Hangzhou, China, 1988.

[13] L.G. Hepler, J. Am. Chem. Soc. 85 (1963) 3089.

[14] Xingen-Hu, Shuqin Li, Ruisen Lin, Hanxing Zong, Thermochimica Acta, 1998, in press.