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Enthalpies and entropies of dissociation of mono-substituted amino benzoic acids in water–ethanol mixtures at 298.15 K

Xingen Hu[a,*], Guiming Luo[b], Fumin Pan[b], Li Yu[b], Qufei Li[b], Yulin Liang[b], Wenjun Fang[b], Ruisen Lin[b]

[a] *Department of Chemistry, Wenzhou Normal College, Wenzhou 325027, PR China*
[b] *Department of Chemistry, Zhejiang University, Hangzhou 310027, PR China*

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Abstract

The dissociation enthalpies of *o*-, *m*-, *p*-amino benzoic acid in water–ethanol mixtures ranging from pure water up to 0.477 molar fraction of ethanol have been determined at 298.15 K by the method of mixing-flowing microcalorimetry. Combined with the available values of Gibbs free energy reported in the literature, the corresponding values of dissociation entropy have been calculated. The enthalpic and entropic effects arising from solvent and substituent have been discussed in terms of solute-solvent interaction and tautomeric equilibrium.

Keywords: Mono-substituted amino benzoic acids; Water–ethanol mixtures; Dissociation enthalpies; Dissociation entropies

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1. Introduction

Investigations on the entropic and enthalpic properties of dissociation processes of mono-substituted benzoic acid isomers in water–organic solvent mixtures are very important for correct understanding their acidic behavior [1–5]. Mono-substituted amino benzoic acids are similar to amino acids in molecular structure, but it is not very clear whether they dissociate in the manner of typical zwitterion in aqueous solutions especially in aqueous organic solvents or not [6]. Therefore in this paper dissociation enthalpies of the two functional groups of mono-substituted *o*-, *m*- and *p*-amino benzoic acids in water–ethanol mixtures have been determined by precise mixing-flow microcalorimetry. Combined with the values of Gibbs free energy, the values of dissociation entropy have been calculated. The dissociation thermodynamic behavior has been discussed from the point of view of solvent and substituent effects.

2. Experimental

2.1. Instrument

The calorimetric instrument is the flow-mixing determination system of LKB-2277 bioactivity monitor (Sweden). The detection limit of thermal power is 0.5 μW. The determination precision is 0.2% (range of 300 W). The precision of electric corrector is ~0.1% (100 W thermal power) and that of constant temperature control is $\sim 5 \times 10^{-4}$ K. The reaction solutions were pumped through the mixing-flow vessel of the calorimeter in uniformed speed using a pair

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* Corresponding author.
E-mail address: kuzhou_2277@163.com (X. Hu).

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of LKB-2132 microperpex peristaltic pumps. The flow rates were corrected by weighing samples (The stability of flow rates is ~0.2%).

2.2. Reagents

Aniline (>99.5%, from Sigma) was used without further purification. *o*-Amino benzoic acid (C.P., >99.0%, from Jiangsu Chemicals Factory), *m*-amino benzoic acid (C.P., >98.0%, from Beijing Chemical Co.) and *p*-amino benzoic acid (A.R., >99.5%, from Shanghai Wulian Chemical Plant) were recrystallized from water–ethanol mixture and dried in infrared oven for 48 h and then were stored over P_2O_5 in a vacuum desiccator. Their melting points were checked prior to use (*o*-amino benzoic acid, 145.2; *m*-amino benzoic acid, 173.4; *p*-amino benzoic acid: 189.3 °C). NaOH (G.R.), $HClO_4$ (A.R.), anhydrous ethanol (G.R.). Water–ethanol mixtures were prepared using twice distilled and deionized water by weight. The mole fraction range of ethanol is 0–0.477.

The solutions of aniline and three amino benzoic acids were prepared directly using mixing solvent by weight. NaOH and $HClO_4$ solutions were prepared by weight using the aqueous solutions with known molarities and densities and anhydrous ethanol.

2.3. Methods

In the water–ethanol mixture of mole fraction x the two dissociation processes of amino benzoic acid cation $H_3{}^+N\Phi CO_2H$ can be expressed as

$$\begin{aligned} &H_3{}^+N\Phi CO_2H + H_2O \\ &\quad \to H_2N\Phi CO_2H + H_3{}^+O, \qquad \Delta H_{i,1} \end{aligned} \tag{1}$$

$$\begin{aligned} &H_2N\Phi CO_2H + H_2O \\ &\quad \to H_2N\Phi CO_2{}^- + H_3{}^+O, \qquad \Delta H_{i,2} \end{aligned} \tag{2}$$

where $\Delta H_{i,1}$ and $\Delta H_{i,2}$ are the apparent enthalpies of dissociation reactions (1) and (2), respectively. The relations between $\Delta H_{i,1}$, $\Delta H_{i,2}$ and $\Delta H^0_{i,1}$, $\Delta H^0_{i,2}$ (standard enthalpies of dissociation) are

$$\Delta H^0_{i,1} = \Delta H_{i,1}\left(\sum b_i \to 0\right) \tag{3}$$

$$\Delta H^0_{i,2} = \Delta H_{i,2}\left(\sum b_i \to 0\right) \tag{4}$$

in which b_i represents the molality of each reactant.

2.3.1. The determination method of $\Delta H^0_{i,1}$

In the mixed solvent of a certain composition (x), the reaction thermal power P_1 of amino benzoic acid (b_1) and perchloric acid (b_2) as well as their own dilution thermal powers (W_1, W_2) were determined.

$$\begin{aligned} &H_2N\Phi CO_2H + HClO_4 \\ &\quad \to [H_3{}^+N\Phi CO_2H][ClO_4{}^-], \qquad P_1 \end{aligned} \tag{5}$$

Control $b_2 \gg b_1$ so that the reaction can proceed completely. Since reaction (5) turns out to be the reverse reaction of reaction (1), we obtain

$$\Delta H_{i,1} = -\frac{(P_1 - W_1 - W_2)((b_1 M_1/1000) + 1)}{f_1 b_1 (1 - \delta_1)} \tag{6}$$

where b_1 and f_1 are the molality and mass flow rate of amino benzoic acid solution, respectively, M_1 is the molar mass of amino benzoic acid δ_1 is the dissociation degree of $H_3{}^+N$ group under the reaction condition, which can be evaluated from the corresponding dissociation equilibrium constant [7]. At a fixed concentration of $HClO_4$ (b_2), reaction enthalpies ($\Delta H_{i,1}$) of amino benzoic acid of at least five different concentrations (b_1) from diluted to concentrated have been determined, and for each concentration (b_1) twice parallel determinations were required to obtain the average value. Then the reaction enthalpies ($\Delta H_{i,1}$) were extrapolated to infinite dilution of amino benzoic acid to obtain an extrapolated value of reaction enthalpy. With the change of concentration of $HClO_4$ (b_2), different extrapolated values of enthalpy were gained. Therefore the second extrapolation was conducted between the first extrapolated values of reaction enthalpy and the concentrations of $HClO_4$ (b_2). The finally extrapolated value of enthalpy was regarded as the first standard dissociation enthalpy ($\Delta H^0_{i,1}$).

2.3.2. The determination method of $\Delta H^0_{i,2}$

The thermal powers (P_2, P_3) of neutralization reaction for amino benzoic acid and perchloric acid aqueous solutions of the same concentration (b_1) with sodium hydroxide aqueous solution of certain concentration (b_3) as well as their own dilution thermal powers (W_3, W_4, W_5) were determined in the mixed solvent of a certain composition (x).

$$\begin{aligned} &H_2N\Phi\, CO_2H + NaOH \\ &\quad \to H_2N\Phi\, CO_2Na + H_2O, \qquad P_2 \end{aligned} \tag{7}$$

$$HClO_4 + NaOH \rightarrow NaClO_4 + H_2O, \qquad P_3 \tag{8}$$

Control $b_3 \gg b_1$ so that the reactions can proceed thoroughly. So we obtain

$$\Delta H_{i,2} = \frac{[(P_2 - W_3 - W_5) - (P_3 - W_4 - W_5)] \times ((b_1 M_1/1000) + 1)}{f_1 b_1 (1 - \delta_2)} = \frac{(P_2 - P_3 - W_3 + W_4)((b_1 M_1/1000) + 1)}{f_1 b_1 (1 - \delta_2)} \tag{9}$$

where δ_2 is dissociation degree of CO_2H group under the reaction condition, which can be calculated from the corresponding dissociation equilibrium constant [7]. Similarly, extrapolations have been made twice for $\Delta H_{i,2}$ versus the concentration of amino benzoic acid (b_1) and the concentration of NaOH (b_3). The extrapolated value of enthalpy obtained finally can be considered to be the second standard dissociation enthalpy ($\Delta H^0_{i,2}$).

In order to obtain enthalpies of dissociation of water in water–ethanol mixtures, enthalpies of neutralization (ΔH_n) between $HClO_4$ and NaOH (reaction (8)) have been derived from the same experimental run

$$\Delta H_n = \frac{(P_3 - W_4 - W_5)((b_1 M_2/1000) + 1)}{f_1 b_1} \tag{10}$$

in which M_2 is the molar mass of $HClO_4$. Twice extrapolations have been made for ΔH_n versus the concentration of $HClO_4$ (b_1) and the concentration of NaOH (b_3). Finally, standard dissociation enthalpies of water can be obtained.

$$\Delta H^0_{i,w} = -\Delta H_n \left(\sum b_i \rightarrow 0\right) \tag{11}$$

The determination method of dissociation enthalpy of anilinium is similar to that of the first dissociation process of amino benzoic acid.

It should be noticed that, $HClO_4$ and NaOH are supposed to dissociate fully in the composition range of mixed solvent, and the mixed heats of ion–ion and ion–neutral molecule can be neglected. These are reasonable in dilute solutions with high dielectric constants [8].

3. Results and discussions

The dissociation enthalpies (ΔH^0_i) of water, anilinium and the first and the second dissociation enthalpies ($\Delta H^0_{i,1}$, $\Delta H^0_{i,2}$) of *o*-, *m*- and *p*-amino benzoic acids in water–ethanol mixtures of different compositions are shown in Tables 1–5, along with the corresponding values of Gibbs free energy under the work solvent compositions calculated from the dissociation equilibrium constants reported in the literature [7], and the corresponding values of dissociation entropy calculated. The dissociation enthalpies and entropies of benzoic acid in the same mixed solvent have been already reported [5]. The enthalpies of dissociation of water in the mixed solvents obtained in this work are in good agreement with those reported in [9].

3.1. Solvent effects

Solvent effects can be described by thermodynamic functions of transfer for dissociation [10]

$$\delta_S \Delta X^0_i = \Delta X^0_i \text{ (in water–ethanol mixture)} - \Delta X^0_i \text{ (in water)} \tag{12}$$

in which X represents thermodynamic functions G, H and S.

Figs. 1–6 show the trends of thermodynamic functions of transfer for the first and the second dissociations of the three isomers of amino benzoic acid, along with those of benzoic acid and anilinium in the same mixed solvents.

From the variations of Gibbs free energy of transfer with the compositions of water–ethanol mixed solvent,

Table 1
Enthalpies of dissociation of water in water–ethanol mixtures at 298.15 K

x_{EtOH}	$\Delta H^0_{i,w}$ (kJ mol^{-1})	
	This work	Ref. [9]
0.000	55.65 ± 0.23	55.59
0.042	56.53 ± 0.17	56.42
0.089	56.72 ± 0.21	56.89
0.144	55.67 ± 0.31	55.70
0.207	51.79 ± 0.15	51.87
0.281	48.33 ± 0.19	48.29
0.370	43.16 ± 0.11	43.21
0.477	37.53 ± 0.08	37.46

Table 2
Thermodynamic functions of dissociation of anilinium in water–ethanol mixtures at 298.15 K

x_{EtOH}	ΔG_i^0 (kJ mol^{-1})	ΔH_i^0 (kJ mol^{-1})	ΔS_i^0 (J K^{-1} mol^{-1})
0.000	26.20	33.72 ± 0.15	25.22
0.042	25.23	29.00 ± 0.13	12.64
0.089	24.65	27.86 ± 0.14	10.77
0.144	23.92	26.60 ± 0.09	8.99
0.207	23.07	24.66 ± 0.11	5.33
0.281	22.04	22.38 ± 0.08	1.14
0.370	21.65	20.72 ± 0.12	−3.12
0.477	21.29	19.08 ± 0.07	−7.41

it can be seen that the first dissociation behavior of the three isomers of amino benzoic acid is similar to that of anilinium (Fig. 1), while the second dissociation behavior is similar to that of benzoic acid (Fig. 4). The trends of $\delta_S\Delta G_{i,1}^0$ of the three isomers decreasing monotonously with the increasing of x_{EtOH} indicate that the decline of dielectric constants of the mixed solvent is favorable to the dissociation of $NH_3{}^+$ group. On the contrary, the trends of $\delta_S\Delta G_{i,2}^0$ of the three isomers increasing monotonously with the increase of x_{EtOH} indicate that the decline of dielectric constants of the mixed solvent is unfavorable to the dissociation of CO_2H group.

Table 3
Thermodynamic functions of dissociation of *o*-amino benzoic acid in water–ethanol mixtures at 298.15 K

x_{EtOH}	$\Delta G_{i,1}^0$ (kJ mol^{-1})	$\Delta H_{i,1}^0$ (kJ mol^{-1})	$\Delta S_{i,1}^0$ (J K^{-1} mol^{-1})	$\Delta G_{i,2}^0$ (kJ mol^{-1})	$\Delta H_{i,2}^0$ (kJ mol^{-1})	$\Delta S_{i,2}^0$ (J K^{-1} mol^{-1})
0.000	12.22	15.62 ± 0.06	11.40	28.09	11.68 ± 0.07	−55.04
0.042	11.70	12.70 ± 0.11	3.35	28.71	11.22 ± 0.06	−58.66
0.089	11.12	11.93 ± 0.07	2.72	29.80	11.00 ± 0.10	−63.06
0.144	10.39	11.05 ± 0.04	2.21	31.00	10.85 ± 0.09	−67.58
0.207	9.45	3.60 ± 0.02	−19.62	33.10	7.47 ± 0.05	−85.96
0.281	8.16	−3.12 ± 0.02	−37.83	35.11	4.12 ± 0.03	−103.94
0.370	8.02	−4.10 ± 0.01	−40.65	36.84	1.76 ± 0.01	−117.66
0.477	7.82	−5.24 ± 0.05	−43.80	38.53	−0.68 ± 0.00	−131.51

Table 4
Thermodynamic functions of dissociation of *m*-amino benzoic acid in water–ethanol mixtures at 298.15 K

x_{EtOH}	$\Delta G_{i,1}^0$ (kJ mol^{-1})	$\Delta H_{i,1}^0$ (kJ mol^{-1})	$\Delta S_{i,1}^0$ (J K^{-1} mol^{-1})	$\Delta G_{i,2}^0$ (kJ mol^{-1})	$\Delta H_{i,2}^0$ (kJ mol^{-1})	$\Delta S_{i,2}^0$ (J K^{-1} mol^{-1})
0.000	17.75	10.66 ± 0.06	−23.78	27.29	17.62 ± 0.09	−32.43
0.042	17.24	10.51 ± 0.08	−22.57	27.86	16.44 ± 0.06	−38.30
0.089	16.73	9.30 ± 0.03	−24.92	28.55	13.47 ± 0.07	−50.58
0.144	16.27	8.34 ± 0.05	−26.60	29.34	10.42 ± 0.10	−63.46
0.207	15.88	6.08 ± 0.04	−32.87	30.62	7.46 ± 0.06	−77.68
0.281	15.53	4.02 ± 0.04	−38.60	31.46	4.28 ± 0.03	−91.16
0.370	15.48	2.00 ± 0.02	−45.21	33.31	2.80 ± 0.01	−102.33
0.477	14.50	−0.48 ± 0.00	−50.24	35.28	2.02 ± 0.02	−111.55

Table 5
Thermodynamic functions of dissociation of *p*-amino benzoic acid in water–ethanol mixtures at 298.15 K

x_{EtOH}	$\Delta G_{i,1}^0$ (kJ mol^{-1})	$\Delta H_{i,1}^0$ (kJ mol^{-1})	$\Delta S_{i,1}^0$ (J K^{-1} mol^{-1})	$\Delta G_{i,2}^0$ (kJ mol^{-1})	$\Delta H_{i,2}^0$ (kJ mol^{-1})	$\Delta S_{i,2}^0$ (J K^{-1} mol^{-1})
0.000	13.64	18.86 ± 0.12	17.51	28.03	3.00 ± 0.01	−83.95
0.042	12.62	10.52 ± 0.05	−7.04	29.00	4.25 ± 0.02	−83.01
0.089	12.37	7.33 ± 0.03	−16.90	30.83	8.40 ± 0.06	−75.23
0.144	11.70	3.76 ± 0.02	−26.63	32.20	11.72 ± 0.07	−68.69
0.207	10.91	0.22 ± 0.00	−35.85	34.34	8.72 ± 0.07	−85.93
0.281	10.28	−2.64 ± 0.01	−43.33	36.94	6.16 ± 0.04	−103.24
0.370	10.30	−4.76 ± 0.03	−50.51	38.49	4.66 ± 0.05	−113.47
0.477	9.76	−6.46 ± 0.04	−54.40	40.19	3.28 ± 0.02	−123.80

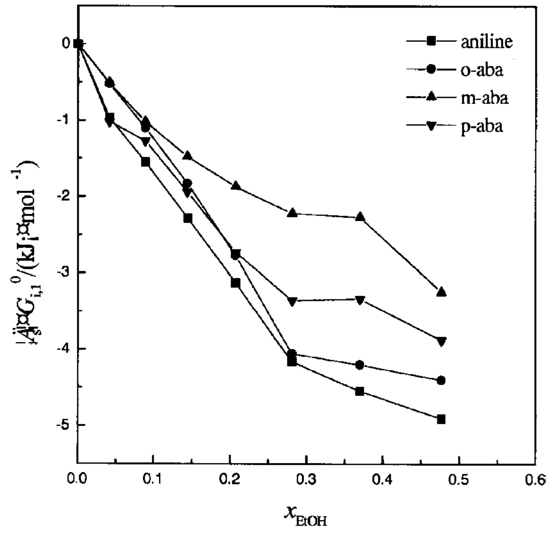


Fig. 1. Transfer Gibbs free energies of reaction (1) ($\delta_S \Delta G^0_{i,1}$) plotted vs. x_{EtOH}.

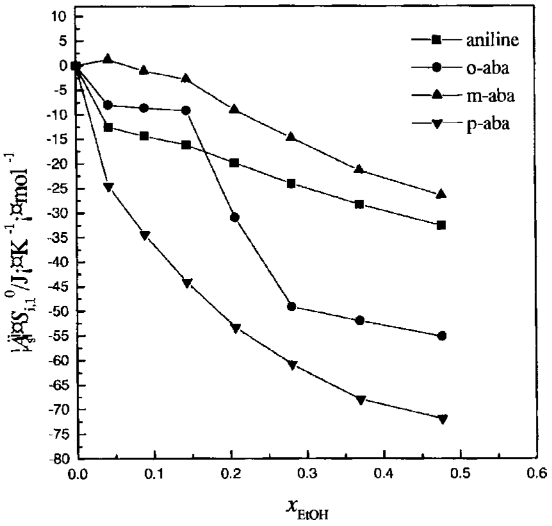


Fig. 3. Transfer entropies of reaction (1) ($\delta_S \Delta S^0_{i,1}$) plotted vs. x_{EtOH}.

However, the variations of enthalpy and entropy of transfer for the first and the second dissociation of the three isomers in water–ethanol mixed solvent with x_{EtOH} are far from simple compared to Gibbs free energy of transfer because they exhibit irregular variation trends (Figs. 2, 3, 5, 6). In the water-rich region of mixed solvent ($0 < x_{EtOH} < 0.2$), the irregular variations of enthalpy and entropy are the most remarkable and the discrepancies of enthalpic and entropic behavior between the three isomers are also notable. On the one hand, this bears relation to the largest structuredness of mixed solvent in the very composition region [11]; on the other hand, this has a concern with

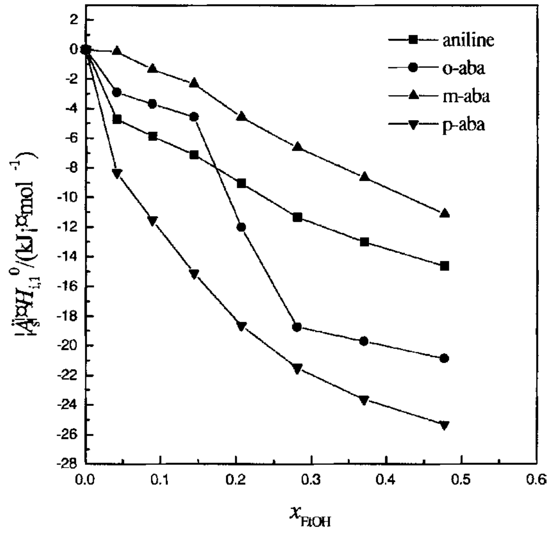


Fig. 2. Transfer enthalpies of reaction (1) ($\delta_S \Delta H^0_{i,1}$) plotted vs. x_{EtOH}.

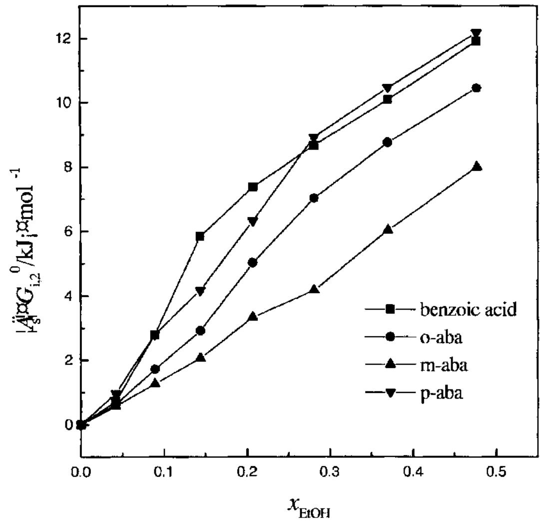


Fig. 4. Transfer Gibbs free energies of reaction (2) ($\delta_S \Delta G^0_{i,2}$) plotted vs. x_{EtOH}.

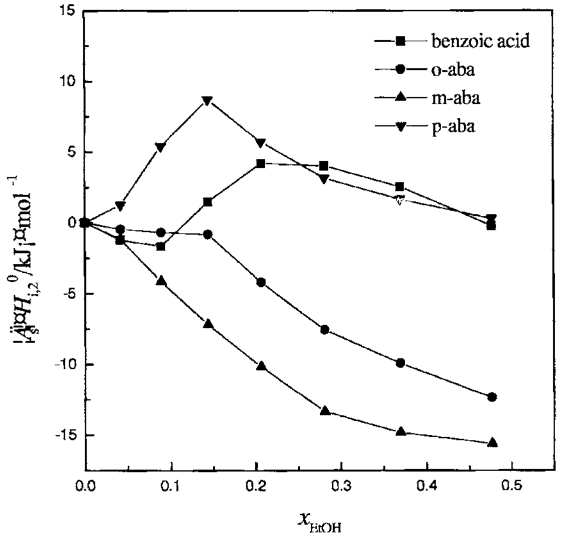


Fig. 5. Transfer enthalpies of reaction (2) ($\delta_S \Delta H_{i,2}^0$) plotted vs. x_{EtOH}.

the disturbance of the tautomeric equilibrium between the zwitterion and neutral molecule of each isomer of amino benzoic acid. Away from this region the variations of enthalpy and entropy of transfer tend towards monotony. This indicates that the structure of mixed solvent begins to break after crossing the largest structural region, and the mixed solvent gradually turns out to be a kind of continuous less structural medium. Simultaneously, the differences of the dissociation behavior of the three isomers diminish by degrees and tend to be identical to each other in the end.

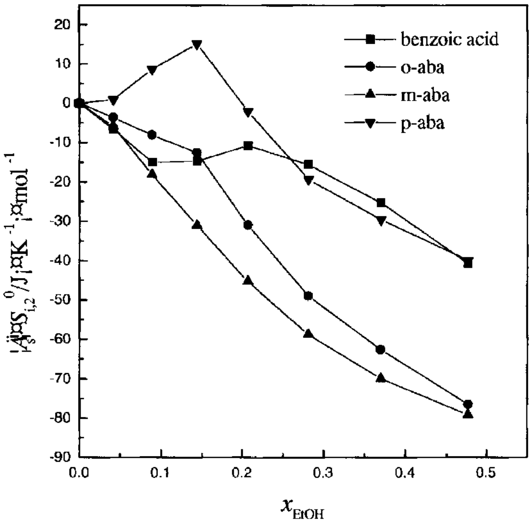


Fig. 6. Transfer entropies of reaction (2) ($\delta_S \Delta S_{i,2}^0$) plotted vs. x_{EtOH}.

Frank and Evans [12] have proposed that zwitterion in aqueous solution has a smaller absolute value of entropy of dissociation. According to a great deal of data collected in the literature [13] about dissociation entropies of organic acids such as aliphatic acids, aromatic acids and amino acids, it can be found that the absolute values of dissociation entropy of neutral acids without charges are always larger, while the absolute values of the first dissociation entropy of typical α-amino acids are about half of the former. This can be explained from the point of view that when neutral acid is dissociated into two ions, more water molecules are "frozen" in aqueous solutions, leading to a larger entropic loss, while the variation of the number of frozen water molecules is not noticeable before and after the dissociation of a zwitterion, and consequently a smaller entropic loss can be found. From Tables 3–5, it can be found that over the whole composition range of the mixed solvent the values of $\Delta S_{i,2}^0$ of *o*- and *p*-isomers are close to the values of neutral acids, while in the water-rich region of the mixed solvent the value of $\Delta S_{i,2}^0$ of *m*-isomer is near to the values of $\Delta S_{i,1}^0$ of typical α-amino acids. It is concluded that over the whole composition range of the mixed solvent the zwitteric properties of *o*- and *p*-isomers of amino benzoic acids are not very evident, that is to say, they exist mainly in the form of neutral molecule; the *m*-isomer behaves obviously as zwitterion in the water-rich region of the mixed solvent, but exists mainly in the form of neutral molecule in ethanol-rich region.

3.2. Substituent effects

Substituent effects on thermodynamic properties of dissociation can be expressed by the following equations

$$\delta_R \Delta X_{i,1}^0 = \Delta X_i^0(\mathrm{R\Phi NH_3}^+) - \Delta X_i^0(\mathrm{\Phi NH_3}^+) \quad (13)$$

$$\delta_R \Delta X_{i,2}^0 = \Delta X_i^0(\mathrm{R'\Phi CO_2H}) - \Delta X_i^0(\mathrm{\Phi CO_2H}) \quad (14)$$

in which X represents thermodynamic functions G, H, and S; R and R′ represent substituents *o*-, *m*-, *p*-CO_2H and *o*-, *m*-, *p*-NH_2 respectively. $\delta_R\Delta X^0_{i,1}$ and $\delta_R\Delta X^0_{i,2}$ equal to the values of thermodynamic functions of the following proton-transfer reactions

$$R\Phi NH_3{}^+ + \Phi NH_2 = R\Phi NH_2 + \Phi NH_3, \qquad \delta_R\Delta X^0_{i,1} \tag{15}$$

$$R'\Phi CO_2H + \Phi CO_2{}^- = R'\Phi CO_2{}^- + \Phi CO_2H, \qquad \delta_R\Delta X^0_{i,2} \tag{16}$$

The above reactions can also be regarded as the transfer process of substituent R (or R′) between $R\Phi NH_3{}^+$ and ΦNH_2 (or between $R'\Phi CO_2H$ and $\Phi CO_2{}^-$).

Because of the symmetry of reactions (15) and (16), the internal entropic changes of them are approximate to zero [14,15]. So the entropic changes of the reactions in solutions arise completely from the variation of reaction medium. As a result, the changes of solute-solvent interaction caused by different positions of substituent can be discussed by $\delta_R\Delta S^0_{i,1}$.

Figs. 7 and 8 describe the trends of $\delta_R\Delta S^0_{i,1}$ and $\delta_R\Delta S^0_{i,2}$ with x_{EtOH}, respectively. $\delta_R\Delta S^0_{i,1}$ equals the entropic change of transfer reaction (15) of carboxyl group (-CO_2H). The values of $\delta_R\Delta S^0_{i,1}$ over the whole mixed solvent composition range are all negative. This indicates that entropic change is unfavorable to the transfer of each carboxyl group in each substituted position. When carboxyl group transfers from the cation of each amino benzoic acid isomer to aniline to produce amino benzoic acid neutral molecule, strong electron-attracting conjugation and inductive effect of carboxyl group (R^-, I^-) make the positive and negative charges in the molecule separate highly from each other. As it has a stronger structure-making ability of solvation, the entropy of the system decreases. Thus, the transfer reaction (15) is an entropy-declining process.

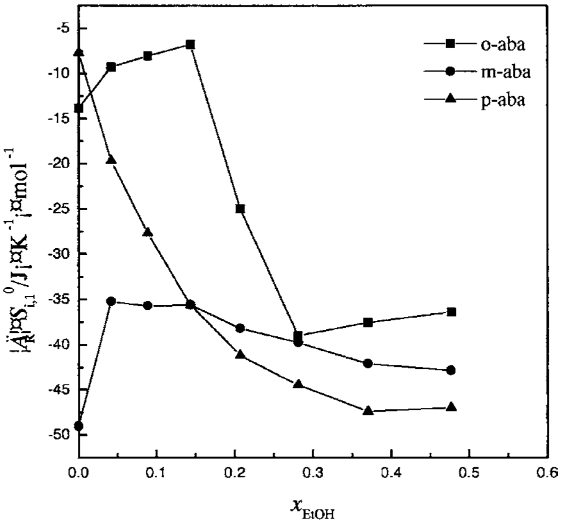


Fig. 7. Entropies of proton-transfer reaction (15) ($\delta_R\Delta S^0_{i,1}$) plotted vs. x_{EtOH}.

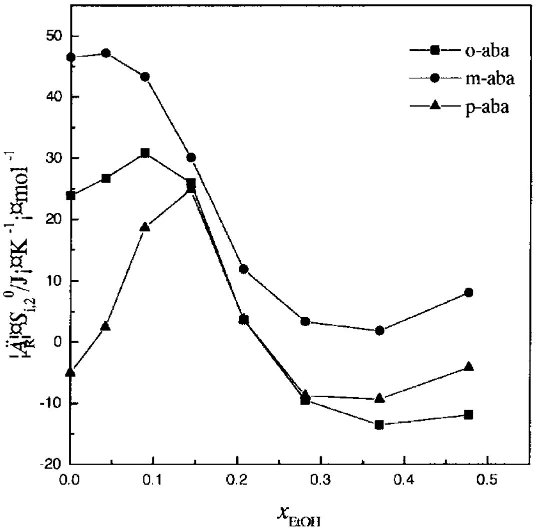
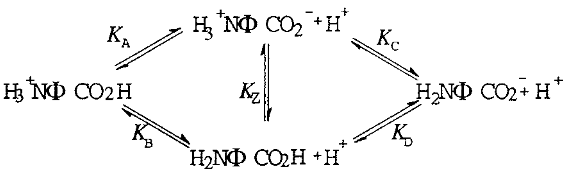


Fig. 8. Entropies of proton-transfer reaction (16) ($\delta_S\Delta S^0_{i,2}$) plotted vs. x_{EtOH}.

When carboxyl group is in different opposition (*o*-, *m*- and *p*-), the variations of $\delta_R\Delta S^0_{i,1}$ with the solvent composition present different characters (Fig. 7). When substituted in p-position, $\delta_R\Delta S^0_{i,1}$ exhibits a trend of monotonous decline. But when substituted in *o*- or *m*-position, $\delta_R\Delta S^0_{i,1}$ goes through a maximum in the water-rich region of the mixed solvent. It has been indicated that in aqueous solutions *p*-amino benzoic acid cation conducts the first dissociation mainly in the way of forming neutral molecule (route B)



K_A, K_B, K_C, K_D-microscopic dissociation equilibrium constants, K_Z-tautomeric equilibrium constants between zwitterion and neutral molecule.

So the first dissociation of *p*-amino benzoic acid cation is similar to anilinium in nature. The first dissociation of *o*- or *m*-isomer cation goes on by route A and there is poor comparison with anilinium. The difference of $\delta_R \Delta S^0_{i,1}$ of the three isomers is very obvious in the water-rich region (Fig. 7). With the increase of x_{EtOH} of the mixed solvent, the trends of $\delta_R \Delta S^0_{i,1}$ of the three isomers become smooth and identical to each other gradually. This indicates that they go by the same route of dissociation in this region (route B).

$\delta_R \Delta S^0_{i,2}$ equals the entropic change of transfer reaction (16) of amino group between neutral molecule $H_2N\Phi CO_2H$ and anion $\Phi CO_2{}^-$.

When amino group transfers from neutral molecule to anion, because of the balance between electron-repulsing resonance and electron-drawing inductive effects (R^+, I^-), the variations of $\delta_R \Delta S^0_{i,2}$ of the three isomers with x_{EtOH} exhibit different characters (Fig. 8).

When amino group is in *m*-position, the notable I^- effect dislocates the negative charge of *m*-$H_2N\Phi CO_2{}^-$ and weakens its structure-making ability of solvation, resulting in the increase of entropic value of the system. So $\delta_R \Delta S^0_{i,2}$ is positive over the whole composition range of the mixed solvent.

When amino group is in *o*-position, steric effect makes anion *o*-$H_2N\Phi CO_2{}^-$ can not be solvated fully even in the water-rich region of mixed solvent, leading to the increase of entropy of the system. However, the effect of intramolecular hydrogen bonding in *o*-anion helps decrease the entropic level of the system. Thus the entropic change of transfer reaction $\delta_R \Delta S^0_{i,2}$ is less positive in water-rich region and even negative beyond this region.

When amino group is in *p*-position, R^+ and I^- effects coexist and compete. In aqueous solution, R^+ effect are marked and predominant, which concentrates the negative charge of anion *p*-$H_2N\Phi CO_2{}^-$ and strengthens its structure-making ability of solvation, resulting in the negative value of $\delta_R \Delta S^0_{i,2}$. In the largest structural region of the mixed solvent, I^- effect is dominant, which dislocates the negative charge of anion *p*-$H_2N\Phi CO_2{}^-$ and greatly weakens its structure-making ability of solvation, resulting in the positive value of $\delta_R \Delta S^0_{i,2}$ in this region.

In the case of *o*- or *p*-substitution, the maximum of $\delta_R \Delta S^0_{i,2}$ appears in the water-rich region of the mixed solvent. This relates obviously to the largest structuredness of the mixed solvent occurring in the region of this composition. Away from this point, $\delta_R \Delta S^0_{i,2}$ of the three isomers present the declining trends with the increase of x_{EtOH}. This can be attributed to the strengthened dispersion force in rich-ethanol region between anion (*o*-$H_2N\Phi CO_2{}^-$, *m*-$H_2N\Phi CO_2{}^-$, *p*-$H_2N\Phi CO_2{}^-$), whose negative charge is dislocated, and the alkyl group of alcohol.

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