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Ionization thermodynamics of weak acids in water/DMF mixtures at 298.15 K

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Abstract

The enthalpies of ionization of acetic, chloroacetic, bromoacetic and iodoacetic acids in water/DMF mixtures were measured at 298.15 K with an LKB 2277 BioActivity Monitor. Solvent and substituent effects are discussed.

Keywords: DMF; Heat of ionization; Thermodynamics; Water; Weak acid

1. Introduction

The study of some halogenated acetic acids in water/*N*,*N*-dimethyl formamide (DMF) mixtures has been the subject of extended research in this laboratory [1,2].

Water, an amphiprotic solvent, has always been considered as a suitable solvent for most reactions. DMF has many uses as a medium for chemical reactions because it is a dipolar aprotic solvent possessing very high permittivity, and is a powerful solvent for many organic and inorganic compounds. In water/DMF mixtures, there are strong hydrogen-bond interactions between water and DMF. The degree of ionization of acids changes significantly with increasing DMF content in mixed solvent. Therefore, water/DMF solutions constitute a very suitable system for studying the solvation of ions and undissociated molecules which is the driving force of ionization processes.

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The substituting groups (Cl, Br and I) of halogenated acetic acids influence the solvation processes of the undissociated molecules and ions differently depending on their inductive effects.

The aim of this work was to determine the enthalpies of ionization of acetic acid and three halogenated acetic acids, and to study the influence of the substituent and the medium on the dissociation of these weak acids.

2. Experimental

The enthalpies of ionization of acetic, chloroacetic, bromoacetic and iodoacetic acids in water/DMF mixtures were measured with an LKB 2277 BioActivity Monitor.

DMF (A.R.) was purified by procedures given in Ref. [3]. Water/DMF mixtures were prepared by weighing purified DMF and CO_2-free, twice-distilled water. The mole fractions of DMF in these mixtures ranged from 0.0 to 0.356 (in 10% increments from 0% to 70% of DMF by weight). Aqueous solutions of 0.1 mol dm^{-3} NaOH and 0.1 mol dm^{-3} $HClO_4$ were prepared from standard solutions. The concentration of NaOH solution was checked by titrating against potassium hydrogen phthalate, and the concentration of $HClO_4$ solution by titrating against the NaOH solution.

Acetic acid was distilled twice. The chloroacetic, bromoacetic and iodoacetic acids were purified by recrystallization from anhydrous benzene and no contamination with other acetic acids was detected by NMR spectroscopic analyses.

The XCH_2COONa (X is Cl, Br, I) solutions were prepared by adding NaOH solutions of known molarity to halogenated acetic acids dissolved in the mixed solvent to give a water/DMF solution at x mole fraction. The concentration of the sodium salt was always in the range 2×10^{-3} to 4×10^{-4} mol dm^{-3}. A certain amount of acid (about 3–4% of the original content) was not converted into the salt and remained as free acid.

The method of measuring the ionization enthalpies of the four acids was as reported in Refs. [2] and [4].

At every mole fraction of the water/DMF mixtures, the heats of ionization of the four weak acids were measured at five different very dilute concentrations and the enthalpies of ionization at infinite dilution for the acids concerned were obtained by graphical extrapolation. All the measurements were performed at 298.15 K.

3. Results and discussion

Table 1 shows the enthalpies of ionization $\Delta_{DIS}H^{\ominus}$ of acetic acid and the three halogen-acetic acids in water/DMF mixtures. The calculated results of Gibbs free energies $\Delta_{DIS}G^{\ominus}$ and entropies of ionization $\Delta_{DIS}S^{\ominus}$ are also given in Table 1.

Table 1
Ionization thermodynamic functions of halogenated acetic acids in water–DMF mixed solvents at 298.15 K

Mole fraction of DMF	0.000	0.026	0.056	0.092	0.136	0.191	0.262	0.356
Acetic acid								
$\Delta_{\mathrm{DIS}}G^{\ominus}$	27.169	28.109	29.195	30.498	32.090	34.080	36.650	40.051
$\Delta_{\mathrm{DIS}}H^{\ominus}$	−0.414	−0.254	−0.674	1.099	1.541	2.146	3.258	5.686
$\Delta_{\mathrm{DIS}}S^{\ominus}$	−92.513	−93.428	−95.660	−98.604	−102.462	−107.108	−111.996	−115.261
Chloroacetic acid								
$\Delta_{\mathrm{DIS}}G^{\ominus}$	16.324	17.235	18.287	19.548	21.090	23.018	25.506	28.800
$\Delta_{\mathrm{DIS}}H^{\ominus}$	−4.566	−3.478	−3.157	−3.032	−2.752	−2.418	−1.923	0.507
$\Delta_{\mathrm{DIS}}S^{\ominus}$	−70.065	−69.472	−71.922	−75.734	−79.967	−85.312	−91.997	−94.896
Bromoacetic acid								
$\Delta_{\mathrm{DIS}}G^{\ominus}$	16.564	17.475	18.528	19.790	21.333	23.262	25.752	29.048
$\Delta_{\mathrm{DIS}}H^{\ominus}$	−4.864	−4.058	−3.467	−2.982	−2.523	−1.800	−0.872	1.564
$\Delta_{\mathrm{DIS}}S^{\ominus}$	−71.869	−72.224	−73.770	−76.378	−80.013	−84.057	−89.296	−92.182
Iodoacetic acid								
$\Delta_{\mathrm{DIS}}G^{\ominus}$	18.122	19.038	20.095	21.364	22.914	24.852	27.353	
$\Delta_{\mathrm{DIS}}H^{\ominus}$	−5.460	−4.325	−3.276	−2.096	−0.810	0.333	2.730	
$\Delta_{\mathrm{DIS}}S^{\ominus}$	−79.094	−78.360	−78.387	−78.684	−79.570	−82.236	−82.587	

Units of $\Delta_{\mathrm{DIS}}G^{\ominus}$, $\Delta_{\mathrm{DIS}}H^{\ominus}$, $\Delta_{\mathrm{DIS}}S^{\ominus}$ are kJ mol^{-1}, kJ mol^{-1} and J mol^{-1} K^{-1}, respectively

Dissociation of weak acids in solutions can be described by the equation

$$\mathrm{HA} + \mathrm{S} = \mathrm{SH}^{+} + \mathrm{A}^{-} \tag{1}$$

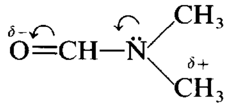
where HA and S represent acid and solvent, respectively.

The effect of solvent on the enthalpies of ionization of weak acids can be defined as

$$\delta\Delta_{\mathrm{DIS}}H^{\ominus} = \Delta_{\mathrm{DIS}}H^{\ominus}(\mathrm{s}) - \Delta_{\mathrm{DIS}}H^{\ominus}(\mathrm{w}) \tag{2}$$

where $\delta\Delta_{\mathrm{DIS}}H^{\ominus}$ represents the solvent effect, and $\Delta_{\mathrm{DIS}}H^{\ominus}(\mathrm{s})$ and $\Delta_{\mathrm{DIS}}H^{\ominus}(\mathrm{w})$ represent the enthalpies of ionization of weak acids in mixed solvents and aqueous solution respectively. The $\delta\Delta_{\mathrm{DIS}}H^{\ominus}$ values of the four acids in water/DMF mixtures at infinite dilutions are plotted against the mole fractions of DMF in water/DMF mixed solvents in Fig. 1. Table 1 and Fig. 1 apparently show that the solvent effects (values of $\delta\Delta_{\mathrm{DIS}}H^{\ominus}$) and the enthalpies of ionization of all four acids increase monotonically with increasing mole fraction of DMF in water/DMF mixtures. This is the result of a decrease in the solvation of the dissociated anions of the weak acids in the water/DMF mixed solvents compared with that in the aqueous solution.

The structure of DMF is



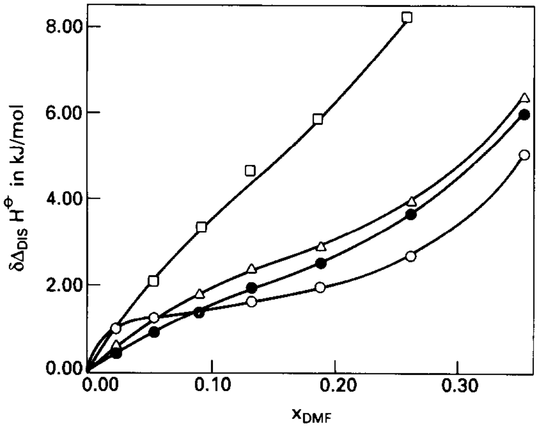


Fig. 1. The effect of composition on the ionization enthalpies of the weak acetic acids at 298.15 K. Key: ●, X = H; ○, X = Cl; △, X = Br; □, X = I.

and the positive electric charge is surrounded by methyl groups. DMF associates mainly with positive ions because of the steric effects of the two methyl groups. Strong hydrogen bonds form between water and DMF molecules in water/DMF mixtures. Hence, the addition of DMF stabilizes the charged particles (XCH_2COO^-). When the acid group ion (XCH_2COO^-) transfers from water to mixed solvent, the solvation of XCH_2COO^- decreases because it does not associate with the DMF molecule. With increasing mole fraction of DMF in the water/DMF mixed solvent, the solvation decreases greatly, and the values of $\delta\Delta_{DIS}H^{\ominus}$ and $\Delta_{DIS}H^{\ominus}$ increase. As a result, the degree of dissociation of weak acids decreases. For the undissociated molecules of weak acids, the increase in the mole fraction of DMF in water/DMF mixtures has little effect on solvation. Nor is solvation of the proton influential. Thus, it follows that the dissociation process is dominated by the stabilization of the conjugated base which is affected by the interactions between the solvent molecule and the base.

Substituent effects can be defined as

$$\delta\Delta_{DIS}S^{\ominus} = \Delta_{DIS}S^{\ominus}(XCH_2COOH) - \Delta_{DIS}S^{\ominus}(CH_3COOH) \quad (3)$$

where $\Delta_{DIS}S^{\ominus}(XCH_2COOH)$ and $\Delta_{DIS}S^{\ominus}(CH_3COOH)$ represent the entropy of ionization of the halogenated acetic acids and acetic acid in mixed solvent, respectively. The $\delta\Delta_{DIS}S^{\ominus}$ of chloroacetic, bromoacetic and iodoacetic acids in water/DMF mixtures at infinite dilutions are plotted against the mole fraction of DMF in water/DMF mixtures in Fig. 2. The negative electric charges on the dissociated halogen-acid group ions (XCH_2COO^-, X is Cl, Br, I) are more dispersed than those on the acetic acid group ions (CH_2COO^-) because halogens have the inductive effect of attracting electrons which is beneficial in stabilizing the anions. But, from the above discussion, when they transfer from water to water/DMF mixture, the solvation decreased. The two opposite effects lead to the phenomenon given in Fig. 2. The change of $\delta\Delta_{DIS}S^{\ominus}$ is $ICH_2COO^- >$

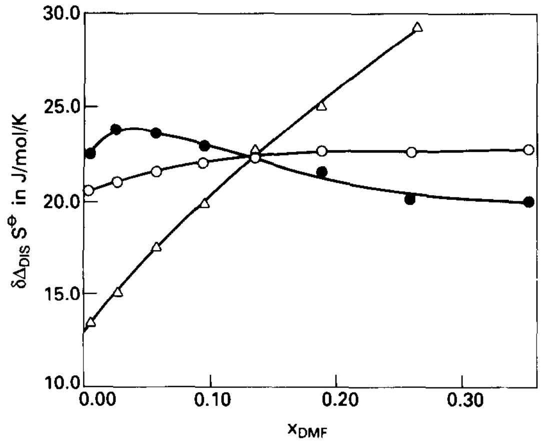


Fig. 2. Substituent effects on the ionization entropies of halogenated acetic acids XCH_2COOH (X is Cl, Br, I) in water–DMF mixtures at 298.15 K. Key: ●, X = Cl; ○, X = Br; △, X = I.

$BrCH_2COO^- > ClCH_2COO^-$, at $x_{DMF} > 0.1$; $ICH_2COO^- < BrCH_2COO^- < ClCH_2COO^-$, at $x_{DMF} < 0.1$. The corresponding acidities of them in water/DMF mixed solvent are $ClCH_2COOH > BrCH_2COOH > ICH_2COOH > CH_3COOH$ at $x_{DMF} > 0.1$; $ICH_2COOH > BrCH_2COOH > ClCH_2COOH > CH_3COOH$ at $x_{DMF} < 0.1$. This result may be related to the microcosmic structure of the water/DMF mixtures, and further investigation is to be desired.

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