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Enthalpic and entropic contributions to dissociation of halogen–acetic acids and linear free energy relationship in EtOH–H_2O mixtures at 298.15 K

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Abstract

On the basis of dissociation enthalpies from micro-calorimetric measurements by using LKB-2277 BioActivity Monitor, along with dissociation equilibrium constants, enthalpic and entropic contributions to substituent effects and solvent effects on the dissociation of acetic acid and three mono-substituted halogen–acetic acids (X–CH_2COOH, X = H, Cl, Br, I) in binary mixtures of EtOH–H_2O have been examined in terms of enthalpic and entropic reaction constants (ρ_H, ρ_S), and enthalpic and entropic substituent constants (σ_H, σ_S). A satisfactory linear free energy relationship (LFER) with the Hammett type equation has been obtained. The reaction constants have been calculated for the different EtOH–H_2O mixtures and several reasonable quantitative equations have been obtained to relate them with the composition or dielectric constant of the mixed solvents.

Keywords: Acid; Dissociation; Enthalpic contribution; Entropic contribution; Mixed solvent; Linear free energy relationship (LFER)

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1. Introduction

Dissociation of an organic acid in mixed solvents is much more complicated than in pure solvents because of both solvent–solvent and solute–solvent interactions. Solvent–solvent interactions may have significant effect on solute–solvent interactions. The solute may be solvated preferentially by any one of the solvents present in the mixture [1]. Christensen et al. [2–5] systematically reported the thermodynamic quantities associated with dilute aqueous solutions from a variety of donor atom types by titration calorimetry. Avedikian and co-workers [6–8] studied solute–solvent interactions in water–organic media from measurements on the dissociation constants and enthalpies for weak acids in water-rich mixtures containing alcohol. Rodante et al. [9–13] carried out systematic calorimetric and thermodynamic investigations of the proton dissociation process of the carboxylate group and the amino group in DMSO-water solutions by means of calorimetric and potentiometric measurements. Previous work [14–18] from this laboratory presented the thermodynamic study of the dissociation of amino acids, substituted acetic acids and substituted benzoic acids in EtOH–H_2O or DMF-H_2O mixed solvents. Ethanol–water binary mixtures have always been considered suitable systems for studying the ionization processes of weak acids and suitable media for chemical reactions since they are powerful solvents for many organic and inorganic compounds. Acetic acid and halogen–acetic acids (X–CH_2COOH, X = H, Cl, Br, I) are very useful reagents in organic synthesis and industrial applications and their thermodynamic or structural data related to the –COOH group or X–C bonds are widely determined [19]. In continuation, the present work further examines the dissociation of acetic acid and three mono-substituted halogen–acetic acids (X–CH_2COOH, X = H, Cl, Br, I) at 298.15 K in EtOH–H_2O binary mixtures ranging in composition of mass fraction w_{EtOH} from 0 to 0.80.

Dissociation process of a substituted acetic acid in solutions can be described simply as:

$$(X\text{–}CH_2COOH)_{solv} = (X\text{–}CH_2COO^-)_{solv} + (H^+)_{solv} \quad (1)$$

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with

$$\Delta_{\mathrm{DIS}}G^0(\mathrm{s}) = \Delta_{\mathrm{DIS}}H^0(\mathrm{s}) - T\Delta_{\mathrm{DIS}}S^0(\mathrm{s}) \tag{2}$$

where $\Delta_{\mathrm{DIS}}G^0(\mathrm{s})$, $\Delta_{\mathrm{DIS}}H^0(\mathrm{s})$ and $\Delta_{\mathrm{DIS}}S^0(\mathrm{s})$ represent the standard Gibbs free energy, enthalpy and entropy for the dissociation of X–CH_2COOH in a given mixed solvent, respectively. For comparison, it is convenient to express the dissociation thermodynamic functions as the difference between the values for X–CH_2COOH (X = H, Cl, Br, I) obtained in a mixed solvent (s) and those for CH_3COOH in pure water (w) at 298.15 K and 101.3 kPa. Hence, we have the following equations:

$$\delta\Delta G^0(\mathrm{s}) = \Delta_{\mathrm{DIS}}G^0(\mathrm{X{-}CH_2COOH, s}) - \Delta_{\mathrm{DIS}}G^0(\mathrm{CH_3COOH, w}) \tag{3a}$$

$$\delta\Delta H^0(\mathrm{s}) = \Delta_{\mathrm{DIS}}H^0(\mathrm{X{-}CH_2COOH, s}) - \Delta_{\mathrm{DIS}}H^0(\mathrm{CH_3COOH, w}) \tag{3b}$$

$$T\delta\Delta S^0(\mathrm{s}) = T\Delta_{\mathrm{DIS}}S^0(\mathrm{X{-}CH_2COOH, s}) - T\Delta_{\mathrm{DIS}}S^0(\mathrm{CH_3COOH, w}) \tag{3c}$$

where the values of $\delta\Delta G^0(\mathrm{s})$, $\delta\Delta H^0(\mathrm{s})$ and $T\delta\Delta S^0(\mathrm{s})$ reflect the total of substituent effects and solvent effects on the dissociation Gibbs free energy, enthalpy and entropy, respectively.

The aim of this work is to investigate the enthalpic and entropic contributions to the dissociation of halogen-acetic acids in EtOH–H_2O mixtures at 298.15 K from the calorimetric data and to give internal quantitative relations for the substituent effects and solvent effects.

2. Experimental

2.1. Materials

Absolute ethanol was used with purity better than 99.8% as claimed by the supplier, Shanghai Chemical Corporation China. It was treated by the recommended procedure given in the literature [20]. Triply distilled water with the specific conductance less than 10^{-6} S cm^{-1} was used. Pure solvents were degassed using an ultrasonic oscillator. Binary mixtures of EtOH–H_2O ($w_{\mathrm{EtOH}} = 0 \sim 0.8$) were prepared by directly weighing the constituent components with a Mettler balance, having a precision of ±0.0001 g. Acetic acid was distilled twice. Chloro-acetic, bromo-acetic and iodo-acetic acids were purified by recrystallization from anhydrous benzene and no contamination with other acetic acids was detected by NMR spectroscopic analyses. Sodium hydroxide solution (fresh, carbonate free, 0.1 mol dm^{-3}) and perchloric acid solution (0.1 mol dm^{-3}) were used. Solutions of the sodium salts of each acid were prepared in initial concentration range from 0.003 to 0.025 mol dm^{-3} with existence of about 3% of extra acetic acid to prevent from the free OH^-.

2.2. Methods

A micro-calorimeter, LKB-2277 BioActivity Monitor, was used in the mode of mixing-flow at 298.15 K. The dissociation enthalpies of organic weak acids in binary mixtures of EtOH–H_2O were measured indirectly from the reaction enthalpies of the corresponding sodium salt solutions with the perchloric acid solution.

$$\begin{aligned}&(\mathrm{Na^+})_{\mathrm{solv}} + (\mathrm{X{-}CH_2COO^-})_{\mathrm{solv}} + (\mathrm{H^+})_{\mathrm{solv}} \\ &\quad + (\mathrm{ClO_4}^-)_{\mathrm{solv}} \rightarrow (\mathrm{X{-}CH_2COOH})_{\mathrm{solv}} + (\mathrm{Na^+})_{\mathrm{solv}} \\ &\quad + (\mathrm{ClO_4}^-)_{\mathrm{solv}} \quad \Delta H(\mathrm{s})\end{aligned} \tag{4}$$

The required sodium salt solution (C_s) and the perchloric acid solution (C_a) were fed continuously by two LKB-2132 peristaltic pumps, respectively, at known rates (f_s for the salt solution and f_a for the acid solution) through the mixing cell in the calorimeter to measure the total heat effect (W), consisting principally of the heat effect due to the liberation of the weak acid ($f_sC_s\Delta H(\mathrm{s})$, $\Delta H(\mathrm{s})$ being the molar enthalpy). Corrections resulting from dilution of the salt solution and of the acid solution during mixing and ionization of the weak acid in the given reaction condition must be performed. Hence, the following expression is obtained:

$$-\Delta_{\mathrm{DIS}}H(\mathrm{s}) = \Delta H(\mathrm{s}) = \frac{(W - Q_s + Q_a)}{f_sC_s(1-\alpha)} \tag{5}$$

where Q_s and Q_a are the respective heat effects of dilution for the salt and the perchloric acid solutions, α is the ionization degree of the weak acid which calculated from the ionization constants. In the procedure for one run of the calorimetric measurements, the solutions through the two peristaltic pumps (A and B) were changed in the following five steps: (a) A(solvent) + B(solvent), establishing baseline, (b) A(solvent) + B($HClO_4$ solution), determining Q_a, (c) A(salt solution) + B($HClO_4$ solution), determining W, (d) A(salt solution) + B(solvent), determining Q_s, and (e) A(solvent) + B(solvent), checking baseline. A typical calorimetric curve is shown in Fig. 1. Duplicate runs at five different salt concentrations for each acetic acid in the given mixed solvent were carried out and extrapolated graphically to obtain the dissociation enthalpy at infinite dilution($\Delta_{\mathrm{DIS}}H^0(\mathrm{s})$), namely the standard dissociation enthalpy, for X–CH_2COOH (X = H, Cl, Br, I).

The dissociation equilibrium constants of these acids in mixed solvents were determined by conductometry according to the Ostwald dilution law. Resistance measurements were carried out on an alternated current bridge. A platinized platinum electrode was used. The conductance cells were calibrated using aqueous KCl solutions. All the solutions were maintained at 25 ± 0.01 °C in a Haake F3-C liquid thermostatic bath.

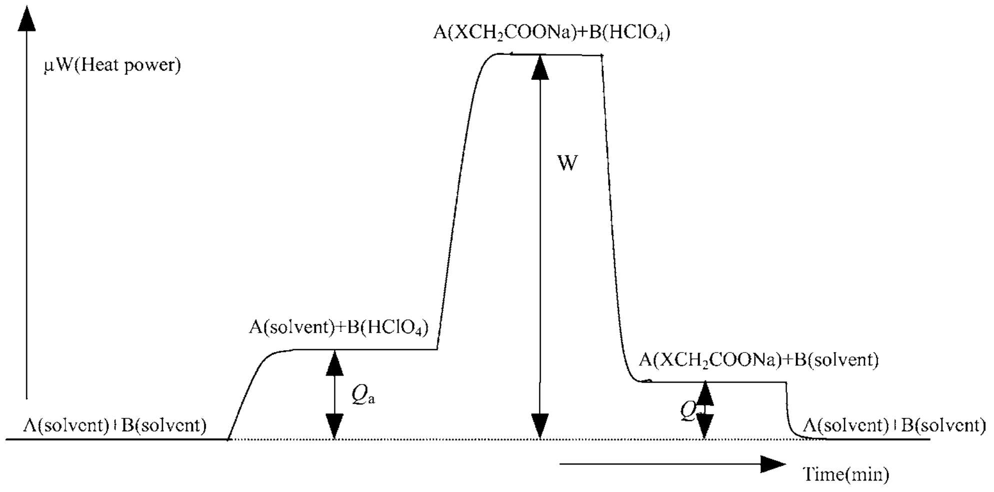

Fig. 1. Calorimetric curve.

3. Results and discussion

3.1. Thermodynamic data

The experimental data of dissociation enthalpy $\Delta_{\mathrm{DIS}}H^0(\mathrm{s})$ and dissociation equilibrium constants $\mathrm{p}K_{\mathrm{a}}^0$ and the values of $\delta\Delta G^0(\mathrm{s})$, $\delta\Delta H^0(\mathrm{s})$ and $T\delta\Delta S^0(\mathrm{s})$ for X–CH_2COOH (X = H, Cl, Br, I) in EtOH–H_2O binary mixtures ranging in composition of mass fraction w_{EtOH} from 0 to 0.80 at 298.15 K are presented in Table 1. Comparison of the values of $\Delta_{\mathrm{DIS}}H^0(\mathrm{s})$ for X–CH_2COOH (X = H, Cl, Br, I) in aqueous solutions [2,4,6,7,14,21–27] is given in Table 2 and for CH_3COOH in EtOH–H_2O mixtures [8,14] is shown in Fig. 2. These experimental data are in reasonable agreement with previously reported data.

3.2. Linear free energy relationship (LFER)

The Hammett equation is the most widespread and best understood linear free energy relationship type equation

$$\log K_{\mathrm{a}} = \log K_{\mathrm{a0}} + \rho\sigma \tag{6}$$

where K_{a} and K_{a0} usually indicates the dissociation constants of mono-substituted benzoic acid and benzoic acid in water at 298.15 K, respectively. ρ is the reaction constant which measures the sensitivity to the effect of substituents and which is dependent on the nature of reaction, solvent and temperature, but not on the substituent. Its value is assumed to be equal to 1 in pure water at 298.15 K and 101.3 kPa. σ is the Hammett substituent constant which is originally assumed to be dependent on the position of the

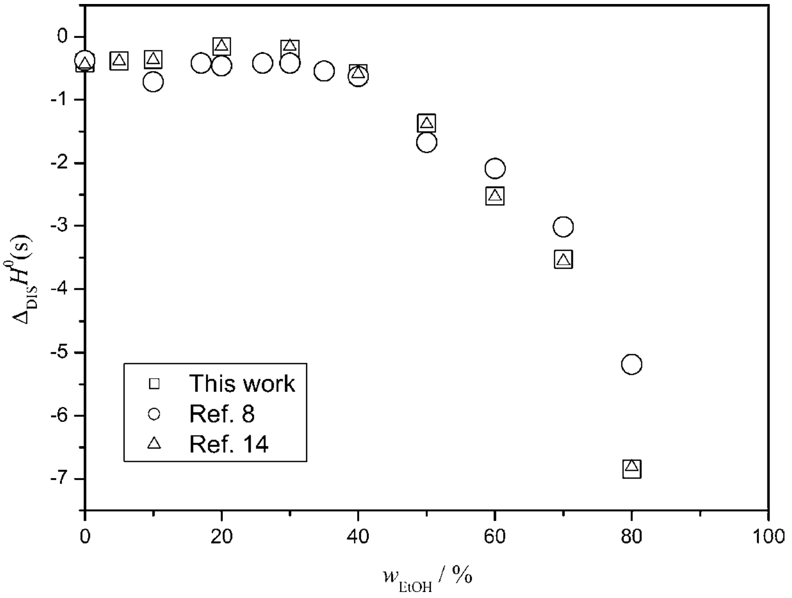

Fig. 2. Comparison of $\Delta_{\mathrm{DIS}}H^0(\mathrm{s})$ values for CH_3COOH in EtOH–H_2O mixtures.

Table 1
Values of $\Delta_{\mathrm{DIS}}H^0(\mathrm{s})$, $\mathrm{p}K_\mathrm{a}^0$, $\delta\Delta G^0(\mathrm{s})$, $\delta\Delta H^0(\mathrm{s})$ and $\delta\Delta S^0(\mathrm{s})$ for dissociation of X–CH_2COOH (X = H, Cl, Br, I) in EtOH–H_2O binary mixtures at 298.15 K

w_{EtOH}	CH_3COOH	$ClCH_2COOH$	$BrCH_2COOH$	ICH_2COOH
$\Delta_{\mathrm{DIS}}H^0(\mathrm{s})$ (kJ mol^{-1})				
0.00	−0.414 ± 0.004	−4.566 ± 0.032	−4.864 ± 0.039	−5.460 ± 0.002
0.05	−0.382 ± 0.006	−4.079 ± 0.031	−4.396 ± 0.013	−5.053 ± 0.034
0.10	−0.358 ± 0.003	−3.696 ± 0.013	−4.320 ± 0.030	−4.852 ± 0.001
0.20	−0.156 ± 0.008	−3.695 ± 0.002	−4.017 ± 0.034	−4.307 ± 0.028
0.30	−0.193 ± 0.003	−3.811 ± 0.004	−3.896 ± 0.037	−3.122 ± 0.022
0.40	−0.587 ± 0.002	−4.209 ± 0.026	−3.696 ± 0.016	−2.056 ± 0.010
0.50	−1.373 ± 0.004	−4.997 ± 0.020	−4.060 ± 0.052	−2.353 ± 0.023
0.60	−2.528 ± 0.026	−6.239 ± 0.059	−5.355 ± 0.061	−3.466 ± 0.001
0.70	−3.529 ± 0.004	−8.091 ± 0.060	−7.382 ± 0.006	−5.680 ± 0.013
0.80	−6.851 ± 0.047	−10.359 ± 0.040	−9.898 ± 0.059	−7.953 ± 0.020
$\mathrm{p}K_\mathrm{a}^0$				
0.00	4.759	2.859	2.902	3.174
0.05	4.870	2.952	2.993	3.265
0.10	4.993	3.035	3.077	3.347
0.20	5.254	3.224	3.265	3.535
0.30	5.560	3.441	3.483	3.751
0.40	5.910	3.688	3.729	3.998
0.50	6.321	3.963	4.005	4.273
0.60	6.816	4.268	4.309	4.579
0.70	7.411	4.601	4.643	4.913
0.80	8.150	4.963	5.006	5.277
$\delta\Delta G^0(\mathrm{s})$ (kJ mol^{-1})				
0.00	0.00	−10.85	−10.61	−9.05
0.05	0.63	−10.32	−10.08	−8.53
0.10	1.33	−9.84	−9.61	−8.06
0.20	2.82	−8.77	−8.53	−6.99
0.30	4.57	−7.52	−7.29	−5.75
0.40	6.57	−6.12	−5.88	−4.35
0.50	8.92	−4.54	−4.31	−2.77
0.60	11.74	−2.81	−2.57	−1.03
0.70	15.14	−0.90	−0.66	0.88
0.80	19.36	1.17	1.41	2.96
$\delta\Delta H^0(\mathrm{s})$ (kJ mol^{-1})				
0.00	0.00	−4.15	−4.45	−5.05
0.05	0.03	−3.67	−3.98	−4.64
0.10	0.06	−3.28	−3.91	−4.44
0.20	0.26	−3.28	−3.60	−3.89
0.30	0.22	−3.40	−3.48	−2.71
0.40	−0.17	−3.80	−3.28	−1.64
0.50	−0.96	−4.58	−3.65	−1.94
0.60	−2.11	−5.83	−4.94	−3.05
0.70	−3.12	−7.68	−6.97	−5.27
0.80	−6.44	−9.95	−9.48	−7.54
$T\delta\Delta S^0(\mathrm{s})$ (kJ mol^{-1})				
0.00	0.00	6.69	6.16	4.00
0.05	−0.60	6.65	6.10	4.09
0.10	−1.28	6.56	5.70	3.42
0.20	−2.57	5.48	4.93	3.10
0.30	−6.74	4.13	3.81	3.04
0.40	−4.35	2.32	3.49	2.70
0.50	−9.88	−0.04	0.66	0.83
0.60	−13.86	−3.02	−2.37	−2.02
0.70	−18.25	−6.77	−6.30	−6.14
0.80	−25.80	−11.11	−10.89	−10.50

Table 2
Comparison of $\Delta_{DIS}H^0(s)$ values for dissociation of X–CH_2COOH (X = H, Cl, Br, I) in aqueous solution at 298.15 K

CH_3COOH		$ClCH_2COOH$		$BrCH_2COOH$		ICH_2COOH	
$\Delta_{DIS}H^0(s)$ (kJ mol^{-1})	Ref.	$\Delta_{DIS}H^0(s)$ (kJ mol^{-1})	Ref.	$\Delta_{DIS}H^0(s)$ (kJ mol^{-1})	Ref.	$\Delta_{DIS}H^0(s)$ (kJ mol^{-1})	Ref.
−0.414 ± 0.004	This work	−4.566 ± 0.032	This work	−4.864 ± 0.039	This work	−5.460 ± 0.002	This work
−0.08 ± 0.21	[2]	−4.69	[2]	−5.19	[2]	−5.94	[2]
−0.377	[6]	−4.14 ± 0.17	[4]	−4.60 ± 0.17	[4]	−5.06 ± 0.29	[4]
−0.400	[7]	−3.054	[6]	−2.594	[6]	−4.853	[6]
−0.436 ± 0.014	[14]	−4.630 ± 0.075	[14]	−4.905 ± 0.047	[14]	−5.570 ± 0.040	[14]
−0.418	[21]	−4.812	[21]	−5.184	[25]	−5.925	[25]
−0.59 ± 0.25	[22]	−4.699	[25]			−5.732	[27]
−0.469	[23]	−4.895	[26]				
−0.293	[24]						

substituent and independent of both solvent and temperature. The σ constant, as a numerical quantity characterizing the given substituent, is of considerable importance exceeding the scope of validity of the Hammett equation. Other sets of substituent constants were defined to extend the application scope of the Hammett equation or to interpret the principles of the substituent effects [28].

To have similar values to Hammett σ constants, the inductive substituent constant σ_I for aliphatic organic acids was defined by [29]:

$$\sigma_I = 0.246 \log\left(\frac{K_a}{K_{a0}}\right) \tag{7}$$

where K_a and K_{a0} should be the dissociation constants of substituted acetic acid and acetic acid in water at 298.15 K, respectively. According to the definitions in Eqs. (3a)–(3c), we can use a uniform expression of the Hammett type equation for halogen−acetic acids in different solvents as follows:

$$\frac{-\delta\Delta G^0(s)}{2.303\,RT} = C(s) + \rho(s)\sigma_I \tag{8}$$

along with which the enthalpic contribution and entropic contribution [12] are as the following expressions:

$$\frac{-\delta\Delta H^0(s)}{2.303\,RT} = C_H(s) + \rho_H(s)\sigma_H \tag{9}$$

$$\frac{\delta\Delta S^0(s)}{2.303R} = C_S(s) + \rho_S(s)\sigma_S \tag{10}$$

where $C_H(s) + C_S(s) = C(s)$, $\rho_H(s)\sigma_H + \rho_S(s)\sigma_S = \rho(s)\sigma_I$. $C(s) = -\delta\Delta G^0(CH_3COOH, s)/2.303RT$. All values of $C(s)$, $C_H(s)$ and $C_S(s)$ are constants in a given solvent and are equal to zero in pure water. $\rho_H(s)$ and $\rho_S(s)$ are enthalpic reaction constant and entropic reaction constant, respectively. σ_H and σ_S are enthalpic substituent constant and entropic substituent constant, respectively. Therefore, Eq. (8) is rewritten in the following form:

$$\frac{-\delta\Delta G^0(s)}{2.303\,RT} = C(s) + \rho_H(s)\sigma_H + \rho_S(s)\sigma_S \tag{11}$$

If it is assumed that the Eqs. (12) and (13) originally for substituted benzoic acids are still valid for halogen−acetic acids with σ_I instead of σ, the values of σ_H and σ_S can be calculated [12].

$$\sigma = 0.91\sigma_S - 0.07 \tag{12}$$

$$\sigma_S = -3.6\sigma_H + 0.15 \tag{13}$$

The values of σ_I calculated from experimental equilibrium constants by Eq. (7), σ_H and σ_S calculated from Eqs. (12) and (13) for the halogen−acetic acids are given in Table 3. Positive σ_I values for substituents Cl, Br and I are because of the strong electron withdrawing ability. These substituents can promote the dissociation of organic acids in the mixed solvents.

Fig. 3 shows the changes of $-\delta\Delta G^0(s)/2.303RT$ of X–CH_2COOH (X = H, Cl, Br, I) against σ_I in different EtOH–H_2O mixtures at 298.15 K, in which a bunch of straight lines with different slopes and intercepts are found. $\delta\Delta G^0(s)$ values in Table 1 have been treated mathematically with Eqs. (8) and (11) by linear regression and reaction constants ($\rho(s)$, $\rho_H(s)$ and $\rho_S(s)$) for each solvent are obtained. The correlation results are gathered in Table 4. The values of $C(s)$, $\rho(s)$, $\rho_H(s)$ and $\rho_S(s)$ apparently representing the solvent effects are plotted against the composition of EtOH–H_2O binary mixtures in Fig. 4 and are quantitatively correlated with w_{EtOH} as listed in Table 5 together with the regressive coefficient (R) and the standard deviation (S.D.).

The $\rho(s)$ values range from 4.066 ($w_{EtOH} = 0$) to 6.935($w_{EtOH} = 0.80$) and increase concomitantly with the ethanol content. The values far larger than 1 indicate that a strong sensitivity to substituents is observed for the dissociation of halogen–acetic acids in EtOH–H_2O solvents. The positive values of $\rho(s)$ indicate the greater facilities

Table 3
Inductive substituent constants σ_I, enthalpic substituent constants σ_H and entropic substituent constants σ_S for X–CH_2COOH (X = H, Cl, Br, I)

X	σ_I	σ_I [29]	σ_H	σ_S
H	0	0	0.020	0.077
Cl	0.467	0.47	−0.122	0.590
Br	0.467	0.47	−0.119	0.579
I	0.390	0.40	−0.099	0.505

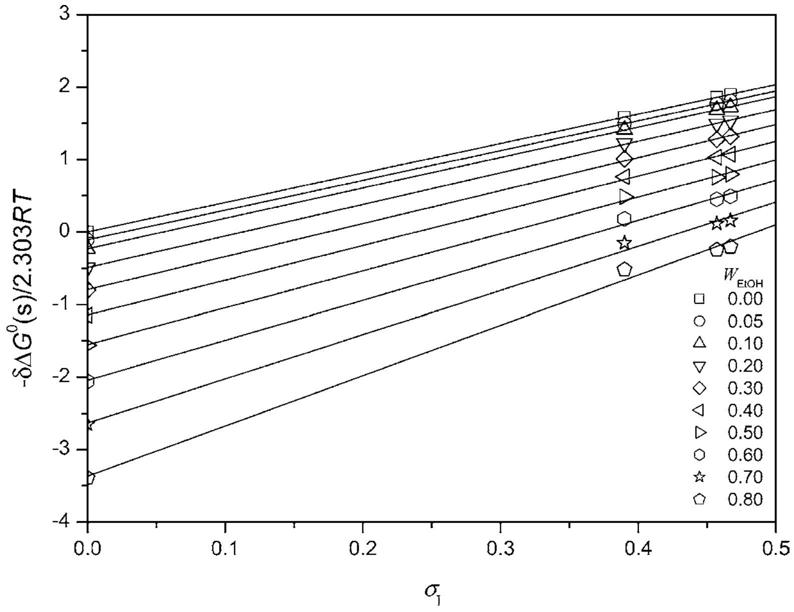

Fig. 3. Plots of $-\delta\Delta G^0(s)/2.303RT$ against σ_I for X–CH_2COOH (X = H, Cl, Br, I) in different EtOH–H_2O mixtures at 298.15 K.

Table 4
Values of $C(s)$, $\rho(s)$, $\rho_H(s)$ and $\rho_S(s)$ for dissociation of X–CH_2COOH (X = H, Cl, Br, I) in different EtOH–H_2O mixtures at 298.15 K

w_{EtOH}	$C(s)$	$\rho(s)$	$\rho_H(s)$	$\rho_S(s)$
0.00	0	4.066 ± 0.002	−6.895 ± 0.009	1.791 ± 0.002
0.05	−0.111 ± 0.002	4.109 ± 0.005	−6.979 ± 0.004	1.808 ± 0.001
0.10	−0.232 ± 0.006	4.196 ± 0.016	−7.151 ± 0.024	1.843 ± 0.005
0.20	−0.492 ± 0.014	4.359 ± 0.036	−7.470 ± 0.059	1.907 ± 0.013
0.30	−0.796 ± 0.022	4.556 ± 0.059	−7.853 ± 0.101	1.985 ± 0.022
0.40	−1.145 ± 0.032	4.787 ± 0.084	−8.302 ± 0.148	2.078 ± 0.032
0.50	−1.553 ± 0.045	5.090 ± 0.118	−8.887 ± 0.208	2.199 ± 0.045
0.60	−2.045 ± 0.062	5.513 ± 0.163	−9.704 ± 0.291	2.369 ± 0.063
0.70	−2.635 ± 0.086	6.096 ± 0.226	−10.826 ± 0.404	2.603 ± 0.088
0.80	−3.368 ± 0.120	6.935 ± 0.316	−12.445 ± 0.568	2.940 ± 0.124

for the development of partial negative charge on the reaction center and also indicate that halogen substituents can enhance the rate of dissociation. The increasing values of $\rho(s)$ are attributed to decreases of the solvation and lowered stabilization of the conjugated base in the direction from water to aqueous organic mixtures. On going from water to mixed solvents, a monotonous decrease of the $C(s)$ value can be observed. Hence, an addition of ethanol into mixed solvents worsens the stabilization of the charged particles formed and thereby lowers the dissociation.

Furthermore, it is found that the plots of $C(s)$, $\rho(s)$, $\rho_H(s)$ and $\rho_S(s)$ against $(\epsilon(s)^{-1}-\epsilon(w)^{-1})$ for the dissocia-

Table 5
Correlation results of $C(s)$, $\rho(s)$, $\rho_H(s)$ and $\rho_S(s)$ with composition or $(\epsilon(s)^{-1}-\epsilon(w)^{-1})$ for dissociation of X–CH_2COOH (X = H, Cl, Br, I) in EtOH–H_2O mixtures at 298.15 K

Equation	R	S.D.
$C(s) = (0.007 \pm 0.006) - (2.408 \pm 0.080)\, w_{EtOH} - (0.009 \pm 0.244)\, (w_{EtOH})^2 - (2.806 \pm 0.201)\, (w_{EtOH})^3$	1.0000	0.008
$\rho(s) = (4.039 \pm 0.019) + (1.957 \pm 0.245)\, w_{EtOH} - (2.719 \pm 0.750)\, (w_{EtOH})^2 + (5.965 \pm 0.617)\, (w_{EtOH})^3$	0.9998	0.023
$\rho_H(s) = -(6.841 \pm 0.037) - (3.840 \pm 0.479)\, w_{EtOH} + (5.311 \pm 1.468)\, (w_{EtOH})^2 - (11.518 \pm 1.208)\, (w_{EtOH})^3$	0.9998	0.046
$\rho_S(s) = (1.780 \pm 0.007) + (0.775 \pm 0.096)\, w_{EtOH} - (1.083 \pm 0.296)\, (w_{EtOH})^2 + (2.395 \pm 0.243)\, (w_{EtOH})^3$	0.9998	0.009
$C(s) = -(0.094 \pm 0.044) - (1.822 \pm 0.060)\, (\epsilon(s)^{-1} - \epsilon(w)^{-1}) \times 10^2$	0.9967	0.080
$\rho(s) = (4.054 \pm 0.018) + (1.393 \pm 0.025)\, (\epsilon(s)^{-1} - \epsilon(w)^{-1}) \times 10^2$	0.9990	0.033
$\rho_H(s) = -(6.878 \pm 0.034) - (2.697 \pm 0.047)\, (\epsilon(s)^{-1} - \epsilon(w)^{-1}) \times 10^2$	0.9990	0.063
$\rho_S(s) = (1.785 \pm 0.007) + (0.557 \pm 0.010)\, (\epsilon(s)^{-1} - \epsilon(w)^{-1}) \times 10^2$	0.9990	0.014

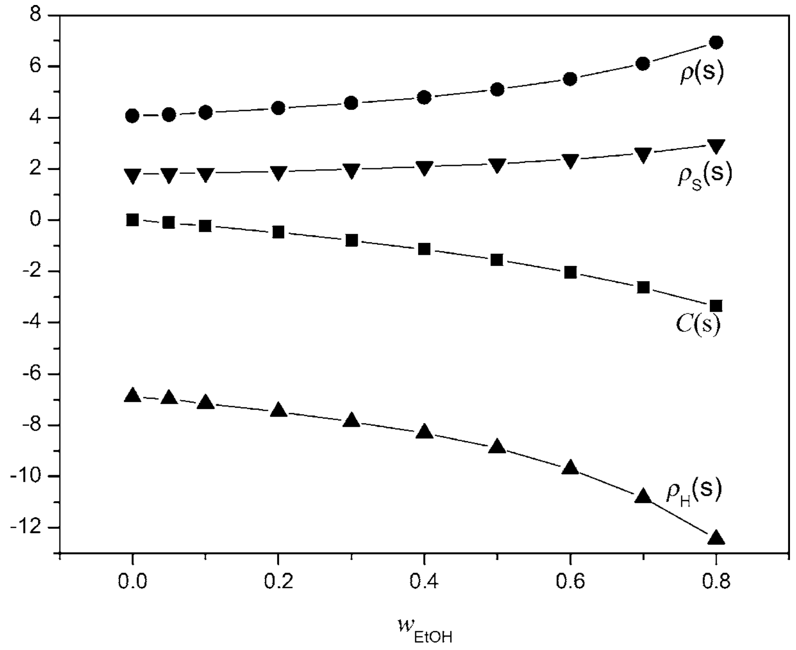

Fig. 4. Plots of C(s), ρ(s), ρ_H(s) and ρ_S(s) for dissociation of X–CH_2COOH (X = H, Cl, Br, I) against w_{EtOH} in EtOH–H_2O mixtures at 298.15 K.

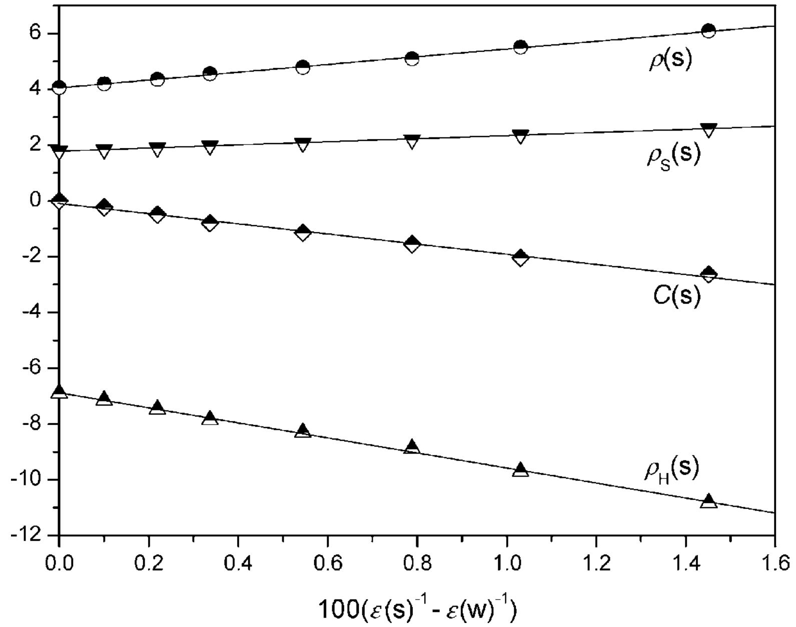

Fig. 5. Plots of C(s), ρ(s), ρ_H(s) and ρ_S(s) against $(\varepsilon(s)^{-1}-\varepsilon(w)^{-1})$ for dissociation of X–CH_2COOH (X = H, Cl, Br, I) in EtOH–H_2O mixtures at 298.15 K.

tion of halogen–acetic acids in EtOH–H_2O binary mixtures at 298.15 K display good linear relationships, which are shown in Fig. 5. The values of dielectric constant of mixed solvent (ϵ(s)) and that of pure water (ϵ(w)) were taken from literature [30].

The regressive equations for the correlation of C(s), ρ(s), ρ_H(s) and ρ_S(s) with $(\epsilon(s)^{-1}-\epsilon(w)^{-1})$ are also listed in Table 5. The combined use of the equations in Table 5 allows us to calculate the $\delta\Delta G^0$(s) or thermodynamic equilibrium constant, and the enthalpic contribution and entropic contribution of a halogen−acetic acid in a binary solvent mixture of EtOH–H_2O.

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