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Enthalpic and entropic contributions to substituent effects on the ionization of *meta*- and *para*-methylbenzoic acids in EtOH–H_2O mixtures at 298.15 K

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Abstract

Enthalpic and entropic contributions to substituent effects on the ionization of *meta*- and *para*-methylbenzoic acids in EtOH–H_2O mixtures have been examined in terms of enthalpic and entropic constants (ρ_H, σ_H and ρ_S, σ_S). The variations of these constants with the molar fractions of the mixed solvents are attributed to the solute–solvent interactions and the structural alteration of the mixed solvents. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Enthalpic contributions; Entropic contributions; *Meta*-methylbenzoic acid; *Para*-methylbenzoic acid; Mixed solvents

1. Introduction

The enthalpic and entropic contributions to substituent effects on the ionization of *meta*- and *para*-halobenzoic acids and *meta*- and *para*-nitrobenzoic acids in the EtOH–H_2O mixtures have been reported recently by us [1,2]. The present work examines the influence of the group –CH_3 (R^+, I^+) on ρ and σ constants for the ionization processes of *meta*- and *para*-methylbenzoic acids at various mole fractions of EtOH–H_2O mixtures.

For proton exchange reaction,

$$(CH_3-\phi COOH)_x + (\phi COO^-)_x = (CH_3-\phi COO^-)_x + (\phi COOH)_x \qquad (1)$$

where x is the mole fraction of ethanol in the mixtures, we have the following equation,

$$-\delta\Delta G^0 = 2.303\,RT\ \rho\sigma \qquad (2)$$

in which $\delta\Delta G^0$ is the standard Gibbs free energy change of the reaction, ρ is the Hammett reaction constant which is dependent on the nature of reaction, solvent and temperature, and σ is the Hammett substituent constant which is originally assumed to be dependent on substituent. The standard ethalpy change for reaction (1) can be obtained as

$$\delta\Delta H^0 = \Delta H_i^0(CH_3-\phi COOH) - \Delta H_i^0(\phi COOH) \qquad (3)$$

in which $\Delta H_i{}^0$ terms represent the ionization enthalpies of weak acids. In the same way, the values of $\delta\Delta G^0$ and $\delta\Delta S^0$ are obtainable. Eq. (2) can be written in the form [3,4]

$$\frac{-\delta\Delta G^0}{2.303\ RT} = \rho\sigma = \rho_H\sigma_H + \rho_S\sigma_S \qquad (4)$$

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Table 1
Thermodynamics of reaction (1) in EtOH–H_2O mixtures at 298.15 K

x_{EtOH}	$\delta\Delta G^0$/kJmol^{-1}		$\delta\Delta H^0$/kJmol^{-1}		$T\delta\Delta S^0$/Jmol^{-1} K^{-1}	
	m-CH_3	*p*-CH_3	*m*-CH_3	*p*-CH_3	*m*-CH_3	*p*-CH_3
0.000	0.48	1.05	−0.24	−0.02	−0.72	−1.07
0.033	0.09	0.72	0.02	0.32	−0.07	−0.40
0.072	0.22	0.79	0.55	1.18	0.33	0.39
0.117	0.47	1.00	1.20	1.97	0.73	0.97
0.170	0.76	1.32	0.86	1.43	0.10	0.11
0.236	0.87	1.29	0.73	0.95	−0.14	−0.34
0.316	1.08	1.60	0.30	0.33	−0.78	−1.27
0.418	0.94	1.62	0.23	0.32	−0.71	−1.30
0.552	1.08	1.99	0.18	0.28	−0.90	−1.71

in which $\rho_H\sigma_H$ and $\rho_S\sigma_S$ are defined by the relations

$$\rho_H\sigma_H = -\frac{\delta\Delta H^0}{2.303\,RT} \tag{5a}$$

$$\rho_S\sigma_S = \frac{\delta\Delta S^0}{2.303\,R} \tag{5b}$$

The values of ρ, ρ_H and ρ_S are assumed to be equal to 1 in pure water at 298.15 K and 101.325 kPa [3,4].

2. Experimental and results

The calorimetric apparatus, LKB-2277 BioActivity Monitor, was used in the mode of mixing-flow at 298.15 K. The experimental procedures for the determination of ionization enthalpies of organic weak acids have been described in detail elsewhere [5]. The results for benzoic and methylbenzoic acids have also been reported by us [6,7].

3. Discussion

The values of $\delta\Delta G^0$, $\delta\Delta H^0$ and $\delta\Delta S^0$ for reaction (1) are given in Table 1. Table 2 gives the values of $\rho\sigma$, $\rho_H\sigma_H$ and $\rho_S\sigma_S$ calculated by Eqs. (2), (5a) and (5b). With the ρ-values for the ionization of benzoic acids at various mole fractions of EtOH reported by Lahiri [8], it is possible to compute the values of σ_m and σ_p. The results are shown in Table 3. If it is assumed that the Eqs. (6a) and (6b) tested in water [9] are still valid over the whole range of mole fractions, the values of σ_H and σ_S can be calculated (Table 3). Furthermore, we can calculate the values of ρ_H and ρ_S by Eqs. (6a) and (6b) These values are gathered in Table 4.

$$\sigma = 0.91\sigma_S - 0.07 \tag{6a}$$

$$\sigma_S = -3.6\sigma_H + 0.15 \tag{6b}$$

For each isomer, internal contributions to the substituent effects are unchangeable from one medium to

Table 2
The values of $\rho\sigma$, $\rho_H\sigma_H$ and $\rho_S\sigma_S$ for the ionization of *m*- and *p*-methylbenzoic acids in EtOH–H_2O mixtures at 298.15 K

x_{EtOH}	*m*-CH_3			*p*-CH_3		
	$\rho\sigma$	$\rho_H\sigma_H$	$\rho_S\sigma_S$	$\rho\sigma$	$\rho_H\sigma_H$	$\rho_S\sigma_S$
0.000	−0.084	0.042	−0.126	−0.184	0.004	−0.188
0.033	−0.016	−0.004	−0.012	−0.126	−0.056	−0.070
0.072	−0.039	−0.096	0.057	−0.138	−0.207	0.069
0.117	0.082	−0.210	0.128	−0.175	−0.345	0.170
0.170	−0.133	−0.151	0.018	−0.231	−0.250	0.019
0.236	−0.152	−0.128	−0.024	−0.226	−0.166	0.060
0.316	−0.189	−0.053	−0.136	−0.280	−0.058	−0.222
0.418	−0.165	−0.040	−0.125	−0.284	−0.056	−0.228
0.552	−0.189	−0.032	−0.157	−0.349	−0.049	−0.300

Table 3
The values of substituent constants σ, σ_H and σ_S for m- and p-methylbenzoic acids in EtOH–H_2O mixtures at 298.15 K

x_{EtOH}	m-CH_3			p-CH3		
	σ	σ_H	σ_S	σ	σ_H	σ_S
0.000	−0.084	0.046	−0.015	−0.184	0.076	−0.125
0.033	−0.020	0.026	0.055	−0.158	0.069	−0.097
0.072	−0.053	0.036	0.019	−0.189	0.078	−0.131
0.117	−0.091	0.048	−0.023	−0.194	0.079	−0.136
0.170	−0.141	0.063	−0.078	−0.246	0.095	−0.193
0.236	−0.138	0.063	−0.075	−0.205	0.083	−0.148
0.316	−0.160	0.069	−0.099	−0.237	0.093	−0.184
0.418	−0.124	0.058	−0.059	−0.214	0.086	−0.158
0.552	−0.170	0.072	−0.110	−0.314	0.116	−0.269

another. Therefore, the variations in the Hammett constants (ρ and σ) and those in enthalpic and entropic constants (σ_H, σ_S, ρ_H, ρ_S) at various mole fractions (Figs. 1 and 2) must be attributed to the change of solute–solvent interactions with structural alteration of the mixed solvents. Experimental evidence on the behavior of binary mixtures of simple aliphatic alcohol and water has indicated that the existence of alcohol molecules causes the structure of water to be enhanced [10]. An explanation of the structural effect is that the hydrocarbon group of the alcohol provides a site for the buildup of an 'iceberg' structure around the alcohol molecule [10]. From the point of view of 'flicking cluster' by Frank and Wen [11], the equilibrium: Bucky Water (iceberg) ↔ Dense Water (monomeric water), shifts to the left in the region rich in water.

The values of ρ and σ are affected by the variation of the solvent composition in different ways (Figs. 1 and 2).

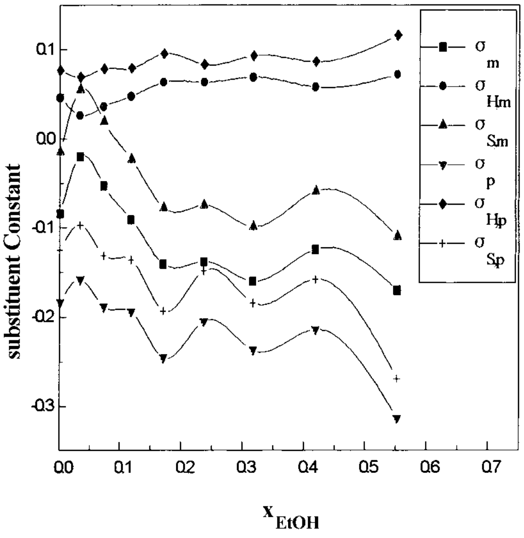

Fig. 1. The variations of substituent constants with x_{EtOH} for ionization of methylbenzoic acids at 298.15 K.

Table 4
The values of ρ, ρ_H and ρ_S for m- and p-methylbenzoic acids in EtOH–H_2O mixtures at 298.15 K

x_{EtOH}	ρ	m-CH_3		p-CH_3	
		ρ_H	ρ_S	ρ_H	ρ_S
0.000	1.00	0.913	8.400	0.053	1.504
0.033	0.80	−0.154	−0.218	−0.812	0.722
0.072	0.73	−2.667	3.000	−2.654	−0.527
0.117	0.90	−4.375	−5.565	−4.367	−1.250
0.170	0.94	−2.397	−0.231	−2.632	−0.098
0.236	1.10	−2.032	0.320	−2.000	0.405
0.316	1.18	−0.768	1.374	−0.624	1.207
0.418	1.33	−0.690	2.119	−0.651	1.443
0.552	1.11	−0.444	1.427	−0.422	1.115

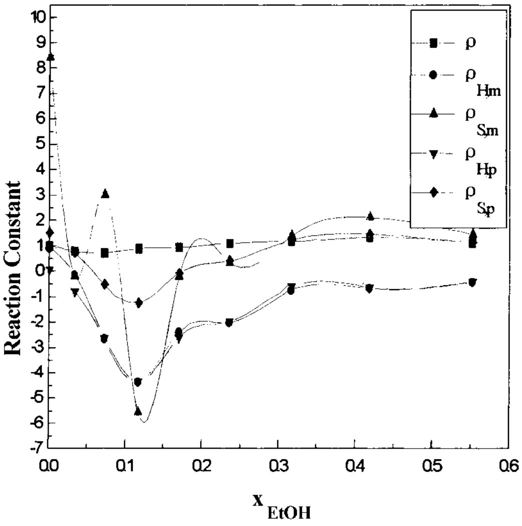

Fig. 2. The variations of reaction constants with x_{EtOH} for ionization of methylbenzoic acids at 298.15 K.

At low mole fractions of ethanol ρ is less than 1 and shows a minimum near 0.100 mole fraction, and then becomes more than 1 beyond about 0.200 mole fraction with a maximum near 0.400 mole fraction. This can probably be correlated with the significant structure and consequent entropy changes in the mixed solvent around 0.100 mole fraction. The increasing positive value of ρ beyond this region indicates the greater facilities for the development of partial negative charge on the reaction center [8]. Little theoretical attempt has been made to elucidate the role of solvents on the parameter ρ [12]. However, it is reasonable to believe that the field and mesomeric effects and the complex interactions that the reactants undergo in solution should be responsible for the change in ρ. The failure in the linear relationship of ρ against the reciprocal of the dielectric constant of solvent (ϵ^{-1}) may be partly due to the changed values of σ in mixed solvents resulted from medium effects [8]. σ is known to change with solvent as evident from the works of Bright and Briscoe [13] and others [14,15]. Considering the strong solvent dependence of Hammett σ values, Hoefnagel and Wepster [16] chose an extended Hammett equation comprising Hansch's hydrophobic constant π as an additional parameter to cover the experimental data for anomalous dissociation constants of benzoic acids in water–organic solvent mixtures,

$$\Delta \log K_i = \rho\sigma + h\pi \tag{7}$$

in which K_i is the dissociation constant, h is a parameter that may be expected to vary with compound series, reaction-type, temperature and solvent.

From theoretical point of view as explained by Dewar and Grisdale [17], σ is dependant on the direct electrostatic (or field) and mesomeric effects, i.e.

$$\sigma^{-} = \frac{F}{\gamma_{ij}} - \frac{M}{\pi_{ij}} \tag{8}$$

in which F and M are constants determining the field and resonance effects, γ_{ij} and π_{ij} are the atom–atom polarizability of the aromatic system and the distance between the points of attachment to the aromatic system of the substituent and reaction center, respectively. Since the direct electrostatic effect is dependant on the effective dielectric constant which definitely changes with solvent system, it leads to a change in σ. But the mesomeric effect probably has little effect on σ. Following Hansen and Hepler's analysis of substituent effects [12], the equation

$$\left(\frac{t_e}{T}\right)\left[-\frac{(a_e + a_r b)}{2.3\,\mathrm{R}}\right] = \left(\frac{t_r}{T}\right)\left[-\frac{(a_e/b + a_r)}{2.3\,\mathrm{R}}\right] = \rho\sigma \tag{9}$$

can be taken for reaction (1). In this equation a_e and a_r are substituent constants for electrostatic field and resonance effects while t_e and t_r are corresponding transmission coefficients. Both substituent constants and t_r are considered to be independent of solvent and temperature, while t_e is taken to depend on both solvent and temperature. The constant $b(=t_r/t_e)$ is a function of solvent, temperature, and pressure. The terms (t/T) are identified with ρ, and the terms containing a_e, a_r, and b are identified with σ. Since b depends on temperature and solvent, the original definition of σ as independent of temperature and solvent cannot be generally and exactly true.

The order of substituent constants is $\sigma_m > \sigma_p$ throughout the whole mole fraction range of EtOH–H_2O mixtures (Table 3). Indeed, the –CH_3 group is electron-donating (I^+, R^+) and thus increases the electron charge density of the reaction center for both the undissociated methylbenzoic acid molecule and its anion. Therefore, the values of σ are negative and the *para*-substituted anion is a stronger base than the *meta*-substituted anion in reaction (1) because of

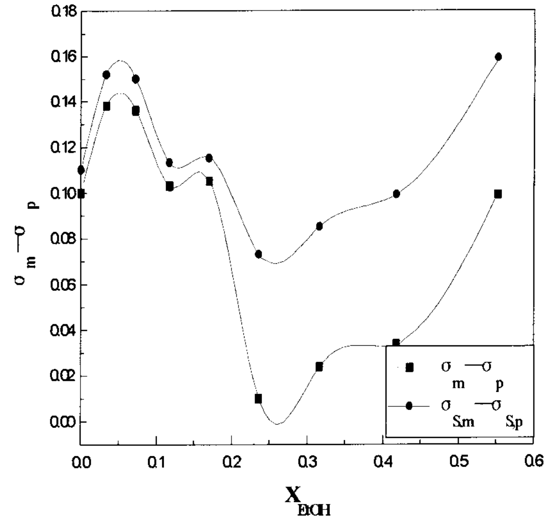

Fig. 3. The variations of $\sigma_m-\sigma_p$ and $\sigma_{S,m}-\sigma_{S,p}$ with x_{EtOH} for ionization of methylbenzoic acids at 298.15 K.

the stronger electron-donating ability of the *para*-CH_3 group which shows a hyperconjugative effect, a special kind of resonance effect primarily involving delocalization of electrons in C–H bonds adjacent to an unsaturated system. If it is assumed that the inductive and field effects (I^+) are approximately the same in both positions, $\sigma_m-\sigma_p$ should be a measure of the resonance effect (R^+) for the *para*-substituted isomer. In the whole composition range of the mixed solvents, the resonance effect does not prevail over the inductive and field effects because $\sigma_m-\sigma_p>0$ (Fig. 3). In the region rich in water ($x_{EtOH}<0.100$), inductive and field effects become especially effective with a maximal value of $\sigma_m-\sigma_p$. When $x_{EtOH}.\approx 0.250$, the inductive and field effects become less effective because of the minimal value of $\sigma_m-\sigma_p$.

The positive values of σ_H indicate that the contribution to $\delta\Delta H^0$ of the interactions between solvent and undissociated molecules is smaller than that of the substituent effects which weaken the oxygen–hydrogen bond in the substituted acids. The fact that the variation of σ_S is more profound than that of σ_H indicates that the external contributions to substituent effects are mostly entropy-controlled and therefore chiefly inductive in character since inductive and field effects are mainly controlled by entropy (Fig. 1). The value of $\sigma_{S,m}-\sigma_{S,p}$, should be a measure of the difference of the inductive and field effects between *meta*- and *para*-CH_3 [3,4]. The variation of $\sigma_{S,m}-\sigma_{S,p}$ with x_{EtOH} must also be ascribed to the change of solute–solvent interactions with structural alteration of the mixed solvents (Fig. 3).

Since internal contributions to substituent effects will not change with medium and the external contributions to substitutent effects are entropy-controlled, the chief intramolecular interaction which controls solute–solvent interactions can be estimated quantitatively as ρ_S. The observed changes in the substituent effects with solvents can thus be conveniently discussed in terms of changes in ρ_S. Considering the fact that the charged components of reaction (1) are anions, the most important property of the solvent should be its acidity, i.e. its ability to solvate anions [18], and thus ρ_S should decrease with an increase in solvent acidity. However, such a type of analysis ignores other important factors affecting ρ_S such as structure-breaking and structure-making effects which accompany solute–solvent interactions. Obviously, a complete analysis must consider all effects [18].

In conclusion, the separation of enthalpic and entropic contributions to substituent effects on the ionization of mono-substituted benzoic acids helps to understand the influence of medium variation on substituent and reaction constants. The medium effects on substituent and reaction constants can be explained in terms of solute–solvent interactions. These interactions are regarded as ‘external’ interactions and are found to be chiefly inductive in character.

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