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Enthalpic and entropic contributions to substituent effects on the ionization of *meta*- and *para*-nitrobenzoic 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*-nitrobenzoic acids in EtOH–H_2O mixtures have been examined in terms of ρ_H, σ_H and ρ_S, σ_S. The variations of ρ_H and ρ_S are attributed to the structural alteration of the mixed solvents. © 1998 Elsevier Science B.V.

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1. Introduction

The enthalpic and entropic contributions to substituent effects on the ionization of *meta*- and *para*-nitrobenzoic acids in EtOH–H_2O mixtures have been examined earlier in our laboratory [1]. The present work examines the influence of the $–NO_2$ (R^-, I^-) group on ρ and σ values, related to the ionization processes of *m*- and *p*-nitrobenzoic acids at various mole fractions of EtOH–H_2O mixtures.

For the proton-exchange reaction

$$(O_2N\text{-}\phi COOH)_x + (\phi COO^-)_x = (O_2N\text{-}\phi COO^-)_x + (\phi COOH)_x \tag{1}$$

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

$$-\delta\Delta G^0 = 2.303RT\rho\sigma \tag{2}$$

The variation of the solvent composition affects the ρ and σ values in different ways. The standard ethalpy for reaction (1) can be obtained as

$$\delta\Delta H^0 = \Delta H_i^0(O_2N\text{-}\phi COOH) - \Delta H_i^0(\phi COOH) \tag{3}$$

In the same way, the $\delta\Delta G^0$ and $\delta\Delta S^0$ values are attainable.

Eq. (2) may be written in the form [2]

$$\delta\Delta G^0/2.303RT = \rho_H\sigma_H + \rho_S\sigma_S \tag{4}$$

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

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

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

where 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 Pa.

2. Experimental and results

The calorimetric apparatus and the experimental procedures for determination of ionization enthalpies of organic acids have been described elsewhere [3]. The results for benzoic and nitrobenzoic acids have also been reported by us [4,5].

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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 calculated by interpolation or extrapolation according to the values reported by Thuaire [6], it is possible to compute the values of σ_m and σ_p. The results are shown in Table 3.

Since the values of σ exhibit limited dependence on the variation of the medium, it seems reasonable to assume that the Eqs. (6a) and (6b), tested in water [7], are still valid over the whole range of mole fractions. Thus, the values of σ_H and ρ_S are also calculated and gathered in Table 3. Finally, we can calculate the values of ρ_H and ρ_S by Eqs. (5a) and (5b). These values are given 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 invariant from one medium to another. The variations in the enthalpic and entropic constants (σ_H,σ_S,ρ_H,ρ_S) at various mole fractions (Tables 3 and 4) are therefore attributable to both, the solute–solvent interactions and structural alteration of the mixed solvents. Experimental evidence on the behavior of binary mixtures of simple aliphatic alcohols and water has indicated that, the presence of alcohol molecules causes the structure of water to be enhanced [8]. An explanation of the structural effect is

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

x_{EtOH}	$\delta\Delta G^0$/kJ mol^{-1}		$\delta\Delta H^0$/kJ mol^{-1}		$\delta\Delta S^0$/J mol^{-1} K^{-1}	
	m-NO_2	p-NO_2	m-NO_2	p-NO_2	m-NO_2	p-NO_2
0.000	−3.97	−4.37	1.48	0.61	18.28	16.70
0.033	−4.76	−5.05	1.72	1.54	21.73	22.10
0.072	−5.09	−5.55	1.83	1.77	23.21	24.45
0.117	−5.34	−5.91	0.99	1.32	21.23	24.24
0.170	−5.63	−6.37	−1.40	−2.30	14.18	23.65
0.236	−5.92	−6.50	−2.65	−3.98	10.97	8.45
0.316	−6.17	−6.51	−3.18	−5.00	10.02	5.06
0.418	−6.31	−6.65	−2.97	−4.65	11.21	6.71
0.552	−6.51	−6.51	−2.87	−4.10	11.47	8.08

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

	m-NO_2			p-NO_2		
x_{EtOH}	$\rho\sigma$	$\rho_H\sigma_H$	$\rho_S\sigma_S$	$\rho\sigma$	$\rho_H\sigma_H$	$\rho_S\sigma_S$
0.000	0.695	−0.259	0.954	0.765	−0.107	0.872
0.033	0.834	−0.301	1.135	0.885	−0.270	1.155
0.072	0.892	−0.321	1.213	0.972	−0.310	1.282
0.117	0.935	−0.173	1.108	1.035	−0.231	1.266
0.170	0.986	0.245	0.741	1.116	0.403	0.713
0.236	1.037	0.464	0.573	1.139	0.697	0.442
0.316	1.081	0.557	0.524	1.140	0.876	0.264
0.418	1.105	0.520	0.585	1.165	0.815	0.350
0.552	1.102	0.503	0.599	1.140	0.178	0.422

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

	m-NO_2			p-NO_2			σ_m−σ_p
x_{EtOH}	σ	σ_H	σ_S	σ	σ_H	σ_S	
0.000	0.695	−0.192	0.841	0.765	−0.213	0.918	−0.070
0.033	0.782	−0.218	0.936	0.830	−0.233	0.989	−0.048
0.072	0.782	−0.218	0.936	0.853	−0.240	1.014	−0.071
0.117	0.771	−0.215	0.924	0.853	−0.240	1.014	−0.082
0.170	0.764	−0.213	0.916	0.865	−0.244	1.027	−0.101
0.236	0.768	−0.214	0.921	0.844	−0.237	1.004	−0.076
0.316	0.763	−0.213	0.915	0.805	−0.225	0.962	−0.042
0.418	0.748	−0.208	0.899	0.789	−0.221	0.944	−0.041
0.552	0.723	−0.200	0.871	0.748	−0.208	0.899	−0.025

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

		m-NO_2		p-NO_2	
x_{EtOH}	ρ	ρ_H	ρ_S	ρ_H	ρ_S
0.000	1.000	1.349	1.134	0.502	0.950
0.033	1.066	1.381	1.213	1.357	1.334
0.072	1.140	1.472	1.296	1.292	1.264
0.117	1.213	0.805	1.199	0.963	1.249
0.170	1.290	−1.150	0.809	−1.652	0.694
0.236	1.350	−2.168	0.622	−2.940	0.440
0.316	1.416	−2.615	0.573	−3.893	0.274
0.418	1.477	−2.500	0.651	−3.688	0.371
0.552	1.525	−2.515	0.688	−3.452	0.469

that, the hydrocarbon group in the alcohol provides sites for buildup of structure around the alcohol molecule [8]. From the point of view of 'flickering cluster', defined by Frank and Wen [9], in the region rich in water, the following equilibrium shifts to the left.

$$\text{Bulky Water (iceberg)} \leftrightarrow \text{Dense Water(monomeric water)} \quad (7)$$

If it is assumed that the inductive and field effects are approximately the same in both positions, $\sigma_m - \sigma_p$ should be a measure of the resonance effect. In the whole range of composition of EtOH–H_2O mixtures, the resonance effect prevails over the inductive effect because $\sigma_m - \sigma_p < 0$ (Table 3). When $x_{\mathrm{EtOH}} \approx 0.17$, the resonance effect is especially effective ($\sigma_m - \sigma_p = -0.101$). The strengthening of the resonance effect may be related to the specific substituent solvation assisted resonance (SSSAR), which leads to the alteration of the electron charge density distribution in the solute molecule [10,11]. Strong hydrogen-bond-acceptor (HBA) substituents give relatively increased acidities of aromatic acids due to the hydrogen-bond-donor (HBD) properties of water, whereas, strong HBD substituents give relatively decreased acidities due to the HBA properties of water. These hydrogen–bond interactions between substituent and water act to modify both, the field/inductive (F) and resonance (R) effects of the substituent.

The negative values of σ_H indicate that, undissociated molecules of nitrobenzoic acids strongly interact with the solvent molecules. The fact that the values of σ_S are larger than σ_H indicates that, the external contributions to substituent effects are mostly entropy-controlled. Since, the field effect is mainly controlled by entropy, the value of $\sigma_{S,m} - \sigma_{S,p}$ is a measure of the difference of the field effects between *m*- and *p*-NO_2. The variation of $\sigma_{S,m} - \sigma_{S,p}$ with x_{EtOH} must be ascribed also to the structural alteration of the mixed solvents.

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References

[1] Nan Yanqing, Lin Ruisen, Yu Qingsen, Acta. Chimica Sinica 55 (1997) 755.
[2] F. Rodante, Thermochimica Acta 31 (1979) 221; 34 (1979) 29.
[3] Hu Ruiding, Yen Wenhsing, Lin Ruisen, Yu Qingsen, Thermochimica Acta 183 (1991) 65.
[4] Xing Zhang, Ruisen Lin, Wenhsing Yan, Acta Chimica Sinica 48 (1990) 295.
[5] Xing Zhang, Ruisen Lin, Hanxing Zong, Wenxing Yan, Acta Chimica Sinica 48 (1990) 28.
[6] M.R. Thuaire, M.G. Champetier, C.R. Acad. Sci. Paris, Sec. C 267 (1968) 993.
[7] T.M. Krygoswski, W.R. Fawcett, Can. J. Chem. 53 (1975) 3622.
[8] F. Franks, D. Ives, Quart. Rev. 20 (1966) 1.
[9] H.S. Frank, W.Y. Wen, Discussions Faraday Soc. 24 (1957) 133.
[10] M. Fujio, R.T. Mclver, R.W. Taft Jr., , J. Am. Chem. Soc. 103 (1981) 4017.
[11] Xingen Hu, Ruisen Lin, Hanxing Zong, Acta Chimica Sinica 55 (1997) 328.