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ENTHALPIC AND ENTROPIC CONTRIBUTIONS TO SUBSTITUENT EFFECTS ON THE IONIZATION OF *META*- AND *PARA*-CHLOROBENZOIC ACIDS IN WATER–DIMETHYLSULFOXIDE MIXTURES AT 25°C

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ABSTRACT

Separate enthalpic and entropic contributions to substituent effects on the dissociation of *m*- and *p*-chlorobenzoic acids in water–dimethylsulfoxide mixtures ranging from 0 to 0.8 mole fraction DMSO are presented.

The effect of the medium on the substituent and reaction constants for the ionization processes is explained in terms of solute–solvent interactions and related structure breaking.

INTRODUCTION

The ionization processes of benzoic and chlorobenzoic acids in water–DMSO mixtures have previously been examined[1, 2].

According to Hammett[3–5], the following equations may be written

$$(\mathrm{Cl{-}PhCOOH})_X + (\mathrm{PhCOO^-})_X = (\mathrm{Cl{-}PhCOO^-})_X + (\mathrm{PhCOOH})_X \quad (1)$$

$$-\delta\Delta G^\circ = 2.303RT\rho\sigma \quad (2)$$

where X (ranging from 0.0 to 0.8) represents the mole fraction of the solvent. The latter interacts differently with each solute species, thus changing in different ways the ρ and σ values. By using experimental ionization values of benzoic[1] and chlorobenzoic acids[2], the standard enthalpy change for reaction (1) is obtained as

$$\delta\Delta H^0 = \Delta H^0_{\mathrm{Cl-PhCOOH}} - \Delta H^0_{\mathrm{PhCOOH}}$$

In the same way, the $\delta\Delta G^\circ$ and $\delta\Delta S^\circ$ values related to process (1) can be obtain. By separating substituent effects into enthalpic and entropic contributions[6], eqn. (2) may be written in the form

$$-\frac{\delta\Delta G^0}{2.303RT} = \rho_\mathrm{H}\sigma_\mathrm{H} + \rho_\mathrm{S}\sigma_\mathrm{S} \quad (3)$$

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

$$\rho_H\sigma_H = -\frac{\delta\Delta H^0}{2.303RT} \tag{4a}$$

$$\rho_S\sigma_S = \frac{\delta\Delta S^0}{2.303R} \tag{4b}$$

In agreement with Hammett, ρ, ρ_H and ρ_S are assumed equal to 1 in water at 25°C and 1 atm.

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus, the preparation of the DMSO–water mixtures and the technique for obtaining the thermodynamic values for benzoic and chlorobenzoic acids have been previously described[1, 2].

RESULTS AND DISCUSSION

The $\delta\Delta H°$, $\delta\Delta G°$ and $\delta\Delta S°$ values of reaction (1) for *m*- and *p*-chlorobenzoic acids are included in eqns. (2), (4a) and (4b), and the values of $\rho\sigma$, $\rho_H\sigma_H$ and $\rho_S\sigma_S$ are reported in Table 1.

On the other hand, it is possible to calculate the σ_m and σ_p values by using the $\rho_{m,p}$ values[7] for the dissociation of benzoic acids at the various DMSO mole fractions (see Table 2). The last values are plotted against X_{DMSO} in Fig. 1.

Since, for each isomer, internal contributions to the substituent effects cannot change, the variations described at the various mole fractions can be attributed both to solute–solvent interactions and structural alteration of the medium.

As inductive effects for chloroderivatives are much greater than resonance

TABLE 1

RESULTS OF APPLICATION OF SEPARATED ENTHALPY–ENTROPY AND NORMAL HAMMETT EQUATIONS TO *m*- AND *p*-CHLOROBENZOIC ACIDS IONIZATION IN WATER–DMSO MIXTURES AT 25°C

X_{DMSO}	*m-Chlorobenzoic acid*			*p-Chlorobenzoic acid*		
	$\rho\sigma$	$\rho_H\rho_H$	$\rho_S\sigma_S$	$\rho\sigma$	$\rho_H\sigma_H$	$\rho_S\sigma_S$
0.0	0.370	−0.073	0.441	0.210	−0.110	0.319
0.1	0.474	0.163	0.310	0.430	0.053	0.365
0.2	0.537	−0.707	1.240	0.490	−0.604	1.097
0.3	0.557	−1.300	1.853	0.470	−2.209	2.670
0.4	0.521	−0.025	0.550	0.360	−2.414	2.450
0.5	0.800	−1.585	2.390	0.520	0.159	0.360
0.6	0.806	−2.675	3.430	0.520	−0.608	1.170
0.7	0.889	−2.073	2.980	0.690	−2.124	2.850
0.8	1.009	−4.263	5.260	0.650	−4.050	4.370

TABLE 2

σ VALUES CALCULATED BY USING THE HAMMETT EQUATION FOR *m*- AND *p*-CHLOROBENZOIC ACIDS IN WATER–DMSO MIXTURES AT 25 °C

X_{DMSO}	*m-Chlorobenzoic acid* σ_m	*p-Chlorobenzoic acid* σ_p
0.0	0.370	0.210
0.1	0.391	0.354
0.2	0.397	0.362
0.3	0.358	0.302
0.4	0.318	0.220
0.5	0.457	0.297
0.6	0.427	0.275
0.7	0.428	0.335
0.8	0.441	0.284

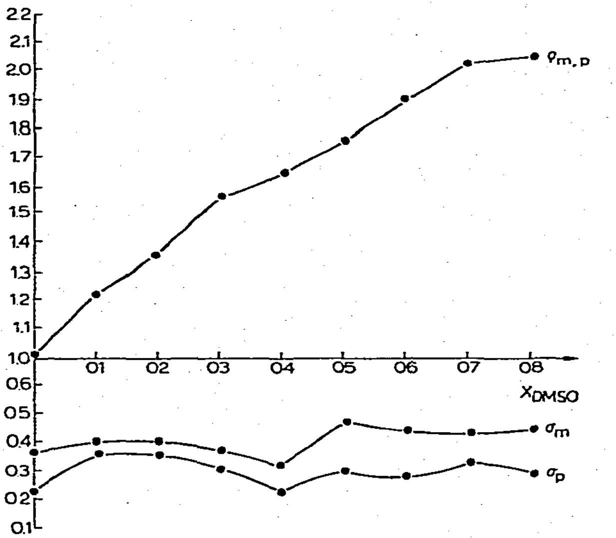

Fig. 1. Variation of the ρ and σ values for *m*- and *p*-chlorobenzoic acids as a function of the mole fraction of DMSO at 25 °C.

effects, one can expect to find σ values that are independent of or only slightly affected by solvent[8].

The order of substituent constant is $\sigma_m > \sigma_p$ throughout the molar fraction range. Indeed, the chlorine atom is electron-withdrawing ($I^- \gg R^+$) thus decreasing the electron charge density of the reaction site for both the undissociated molecule and its anion. Therefore, the σ values are positive and the *m*-anion is a weaker base than the *p*-anion in reaction (1) because of the weaker electron attractive effect of the chlorine atom in the *para* position. This result is in good agreement with the solvation sequence previously proposed for the chloro anions[2].

The reaction constants $\rho_m = \rho_s$ (calculated by using free energy values) fall

TABLE 3

σ VALUES CALCULATED BY USING ENTHALPIC AND ENTROPIC EQUATIONS FOR THE *m*- AND *p*-CHLOROBENZOIC ACIDS IN WATER–DMSO MIXTURES AT 25 °C

X_{DMSO}	*m-Chlorobenzoic acid*		*p-Chlorobenzoic acid*	
	σ_H	σ_S	σ_H	σ_S
0.0	−0.092	0.483	−0.044	0.307
0.1	−0.099	0.506	−0.088	0.466
0.2	−0.101	0.513	−0.090	0.474
0.3	−0.089	0.471	−0.072	0.409
0.4	−0.077	0.426	−0.047	0.318
0.5	−0.119	0.579	−0.070	0.403
0.6	−0.110	0.546	−0.064	0.379
0.7	−0.110	0.548	−0.082	0.445
0.8	−0.114	0.561	−0.066	0.389

TABLE 4

ρ VALUES CALCULATED BY USING THE ENTROPIC EQUATION FOR *m*- AND *p*-CHLOROBENZOIC ACIDS IN WATER–DMSO MIXTURES AT 25 °C

X_{DMSO}	*m-Chlorobenzoic acid*	*p-Chlorobenzoic acid*
	ρ_S	ρ_S
0.0	0.912	1.038
0.1	0.612	0.782
0.2	2.419	2.313
0.3	3.936	6.526
0.4	1.290	7.695
0.5	4.126	0.893
0.6	6.282	3.085
0.7	5.440	6.408
0.8	9.368	11.240

on a straight line due to a decrease of anion solvation which, in turn, is related to an increasing differentiation in the acidity of chloro-substituted and benzoic acids.

Due to the limited dependence of the σ values on the medium effect, it seemed reasonable to assume that the equations tested[6] in water, viz.

$$\sigma = 0.91\,\sigma_S - 0.07$$

and

$$\sigma_S = \mathrm{I}\ 3.6\,\sigma_H + 0.15$$

are valid over the whole range of mole fractions. Values of σ_S and σ_H have been calculated and are given in Table 3. By using the values from Table 1, it is possible to calculate ρ_S values (see Table 4). σ_S and σ_H values are plotted against DMSO mole fraction (Fig. 2), while the ρ_S values are plotted in Fig. 3.

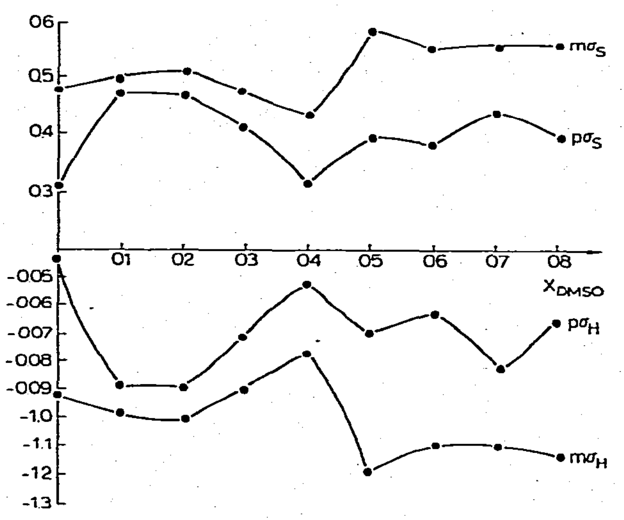

Fig. 2. Variation of the σ_H and σ_S values for *m*- and *p*-chlorobenzoic acids as a function of the mole fraction of DMSO at 25 °C.

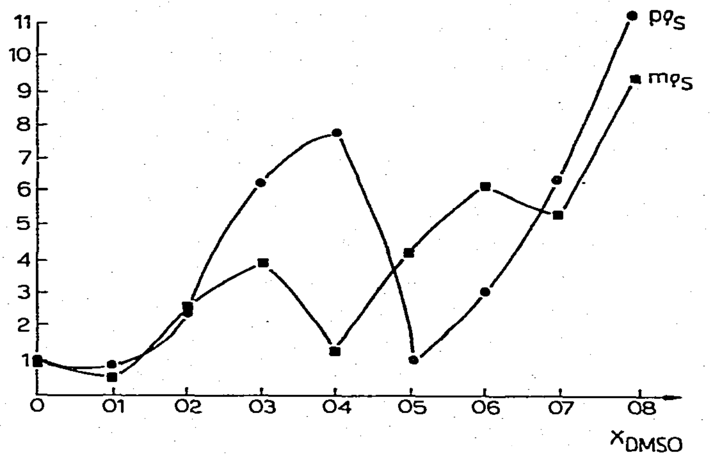

Fig. 3. Variation of the ρ_s values for *m*- and *p*-chlorobenzoic acids as a function of the mole fraction of DMSO at 25 °C.

Negative σ_H values indicate that the contribution to $\delta\Delta H^\circ$ of interaction between solvent and undissociated molecules is greater than the substituent effects which weaken the oxygen–hydrogen bond in the substituted acids.

The greater extent of the effect of the σ_S with respect to the σ_H values indicates that the external contributions are entropy controlled and therefore chiefly inductive in character[6], so that the solute–solvent interactions are exclusively discussed in terms of ρ_S change.

Contrary to the trend of the reaction constants derived from $\delta\Delta G^\circ$ values, the ρ_S constants show a minimum at $X_{DMSO} = 0.4$ and $X_{DMSO} = 0.5$ for *m*- and *p*-chlorobenzoic acids, respectively. This behaviour can be related to a typical feature of DMSO–water solutions[9]. Indeed, at $X_{DMSO} = 0.5$, the maximum structure breaking displayed by the solution increases the solvating power of the mixture towards the anions, so that the maximum solute–solvent interaction is found at the indicated mole fraction.

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