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A STUDY OF SOLVENT AND SUBSTITUENT EFFECTS ON ORGANIC ACIDS. PART II. CONSISTENCY OF A THERMODYNAMIC AND AN ELECTROSTATIC MODEL WITH EXPERIMENTAL RESULTS OF *p*-BENZOIC ACID DERIVATIVES

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ABSTRACT

A thermodynamic and an electrostatic model related to solvent and substituent effects on some organic acids were checked by means of experimental results of *p*-benzoic acid derivatives in DMSO–water solutions. Only the electrostatic model, as could have been expected by virtue of the resonance effect, was found to be consistent with the experimental results.

INTRODUCTION

In the first part of this work [1] a thermodynamic and an electrostatic theory related to substituent and solvent effects on organic acids were checked by means of experimental results of the proton transfer reactions of *m*-benzoic acid derivatives in DMSO–water solutions.

$$\text{R–PhCOOH}_{(s)} + \text{PhCOO}^-_{(s)} = \text{R–PhCOO}^-_{(s)} + \text{PhCOOH}_{(s)} \tag{1}$$

The most important relationships used for this purpose were

$$\delta\Delta G^0 = \delta\Delta H_{\text{in}}(1+\gamma) \tag{2}$$

where γ is a solute–solvent interaction parameter which depends on solvent, temperature, pressure and reaction type, and $\delta\,\Delta H_{\text{in}}$ is an "internal" thermodynamic function

$$\gamma = B\epsilon_i/(1-B)\epsilon_s \tag{3}$$

where B is a dimensionless solvent-independent parameter and ϵ_i and ϵ_s are the dielectric constants of a hypothetical and a real solvent, respectively

$$\frac{\rho_x}{\rho_{x'}} = \frac{1-B(\epsilon_x - \epsilon_i/\epsilon_x)}{1-B(\epsilon_{x'} - \epsilon_i/\epsilon_{x'})} \tag{4}$$

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where ρ_x and $\rho_{x'}$ are the reaction constants of a given reaction, in two solvents, with dielectric constant ϵ_x and $\epsilon_{x'}$, respectively

$$\beta_i = \beta_e - \frac{1+\gamma}{\partial\gamma/\partial T} = T - \frac{1+\gamma}{\partial\gamma/\partial T} \quad (5)$$

where β_i is the isoequilibrium temperature parameter, and β_e is the "environmental" parameter.

Both the models were found to be consistent with the experimental results in some mole fraction intervals. Furthermore, the consistency of the experimental results with the thermodynamic model was related to the absence of the resonance effect in the *meta*-derivatives. Indeed, the simple isoequilibrium relationship is expected to hold true only when the resonance effect is very small compared with the field effect [2].

The experimental values of the ionization of the *p*-chloro-, *p*-nitro- and *p*-hydroxy- derivatives in the same DMSO–water solutions may be a good starting point for a more profound investigation in this respect.

EXPERIMENTAL AND PROCEDURE

The preparation of the DMSO–water solutions and the technique for obtaining the thermodynamic values for the benzoic [3] and substituted benzoic acids [4–6] have been described previously.

RESULTS AND DISCUSSION

As shown previously [7–10], a thermodynamic cycle allows the calculation of a proton transfer process in a solvent s referring to a gaseous initial state, i.e. $\delta\Delta P_i^{g\to s}$. These thermodynamic quantities have been assumed to be a measure of the "environmental" solute–solvent interactions. Bearing in mind that the $\delta\Delta G_{i(g)} = \delta\Delta H_{i(g)}$ values of the proton transfer process in the gaseous phase represent the "internal" solute–solvent interactions [7–9], the γ values of the *para*-derivatives in the whole mole fraction range can be calculated by means of eqn. (2). These values are reported in Table 1 and are plotted against DMSO mole fraction in Fig. 1.

As previously shown [1] for the *meta*-derivatives, the γ values of the chloro- and nitro-derivatives are similar and tend to decrease as the DMSO content increases. Furthermore, the influence of the solvent on the hydroxy-derivative can be represented by the large values of the γ parameter. This may be due to the hydrogen bonding between the hydroxyl group and the solvent molecules, and to the resonance effect, the latter occurring mostly in the 0.45–0.55 mole fraction range.

For the hydroxy-derivative it is also interesting to note that the informa-

TABLE 1

Values of γ for the dissociation of *p*-chloro-, *p*-nitro- and *p*-hydroxybenzoic acid in water–DMSO mixtures at 25°C

X_{DMSO}	*p*-Cl	*p*-NO_2	*p*-OH
0.0	−0.935	−0.907	−1.130
0.1	−0.866	−0.886	−1.145
0.2	−0.848	−0.870	−1.168
0.3	−0.854	−0.855	−1.233
0.4	−0.889	−0.844	−1.185
0.5	−0.839	−0.837	−1.413
0.6	−0.839	−0.823	−1.243
0.7	−0.785	−0.820	−1.263
0.8	−0.798	−0.794	−1.295

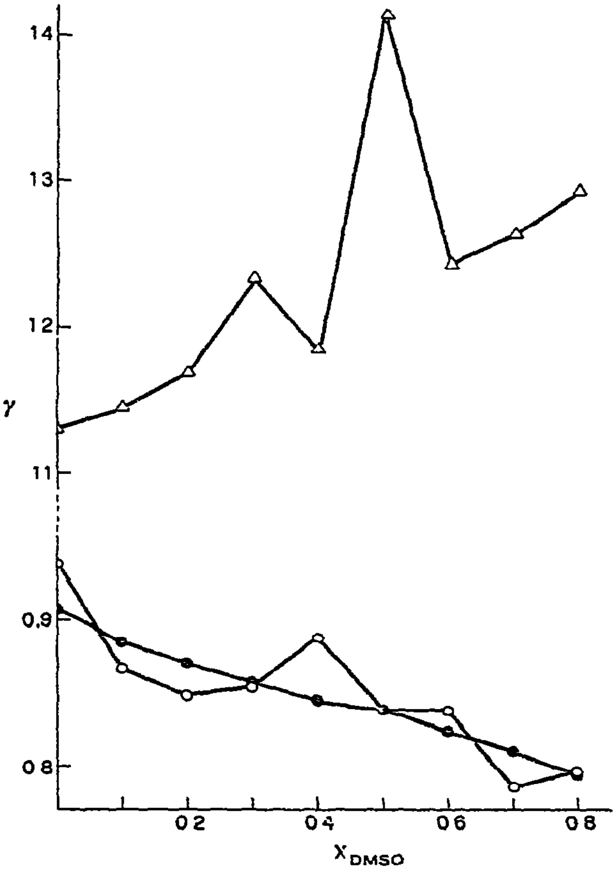

Fig. 1. Variation of the $-\gamma$ values for *p*-chloro- (○), *p*-nitro- (●), and *p*-hydroxybenzoic acid (△) as a function of the mole fraction of DMSO at 25°C.

TABLE 2

Values of ρ/γ for the ionization of *p*-chloro-, *p*-nitro- and *p*-hydroxybenzoic acid in water–DMSO mixtures at 25°C

X_{DMSO}	*p*-Cl	*p*-NO_2	*p*-OH
0.0	1.07	1.10	0.88
0.1	1.40	1.37	1.06
0.2	1.60	1.56	1.16
0.3	1.81	1.81	1.26
0.4	1.85	1.94	1.38
0.5	2.10	2.10	1.24
0.6	2.25	2.30	1.52
0.7	2.62	2.54	1.63
0.8	3.62	3.64	2.23

tion obtained from the γ values is more useful than that obtained from the ρ and ρ_s values. Indeed, the γ values are very close to those [9] of the $T\delta\Delta S^{g\rightarrow s}$ entropic term and very different from the ρ_s terms [11]. This confirms that the $\sigma_s = 0.91\sigma - 0.07$ equation gives very approximate values [9,11] only in the 0.45–0.55 mole fraction range.

The variation of the ρ/γ ratio (see Table 2 and Fig. 2) as a function of the mole fraction shows how the same correlation between the ρ and γ parameters can be assumed for the chloro- and nitro-derivatives.

As eqn. (2) can also be written [1] as

$$\rho\sigma = [C(I+\gamma)/2.303RT]\left[-\delta\Delta H_{in/c}\right] \qquad (6)$$

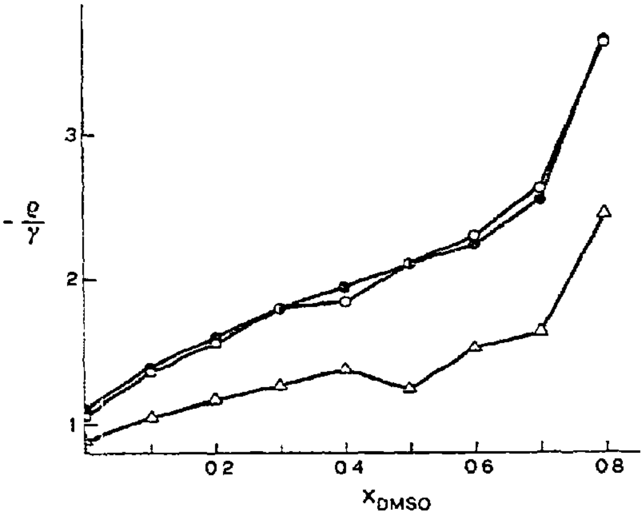

Fig. 2. Variation of the $-\rho/\gamma$ values for *p*-chloro- (○), *p*-nitro- (●), and *p*-hydroxybenzoic acid (△) as a function of the mole fraction of DMSO at 25°C.

TABLE 3

Values of σ calculated using the equation $\sigma = -\delta\Delta H_{\mathrm{in}/C}$ in water–DMSO mixtures at 25°C

X_{DMSO}	p-Cl	p-NO$_2$	p-OH
0.0	0.210	0.757	0.381
0.1	0.356	0.765	0.350
0.2	0.362	0.781	0.364
0.3	0.304	0.761	0.450
0.4	0.218	0.775	0.331
0.5	0.218	0.758	0.691
0.6	0.275	0.763	0.377
0.7	0.336	0.749	0.374
0.8	0.226	0.581	0.299

where $\rho = [C(I+\gamma)/2.303RT]$, and $\sigma = [-\delta\Delta H_{\mathrm{in}/C}]$, values of C and σ can be calculated. The σ values (see Table 3) are very close to those previously calculated using the "normal" Hammett equation [11–13].

Equation (3) gives the values of the B parameter by assuming [1] $\epsilon_i = 2.5$ and $\epsilon_i = 6$. Figure 3 shows that for $\epsilon_i = 2.5$ (chloro and nitro) and $\epsilon_i = 6$ (hydroxy) the B parameter values are constant and nearly equal in the various solutions. Moreover, eqn. (4) allows the calculation of the variation of the ρ_x/ρ_x' ratio in the whole mole fraction range (Table 4, Fig. 4) and, therefore, the difference between the calculated [14] and experimental ratios: $|(\rho_x/\rho_{x'})_{\mathrm{calc}} - (\rho_x/\rho_x')_{\mathrm{exp}}|$. The standard deviation of the differences has been calculated for each derivative. For the chloro-, nitro- and hydroxy-derivatives the standard deviations are 0.08, 0.08 and 0.09, respectively. If the largest differences (the first and the last) are eliminated, the standard

TABLE 4

Values of $\rho_x/\rho_{x'}$ calculated using eqn. (4) for the dissociation of p-chloro-, p-nitro- and p-hydroxybenzoic acid in water–DMSO mixtures at 25°C

$X_{\mathrm{DMSO}}/X'_{\mathrm{DMSO}}$	p-Cl		p-NO$_2$		p-OH	
	$\epsilon_i = 2.5$	$\epsilon_i = 6$	$\epsilon_i = 2.5$	$\epsilon_i = 6$	$\epsilon_i = 6$	$\epsilon_i = 2.5$
0.0/0.1	0.944	0.943	0.975	0.971	0.983	0.989
0.1/0.2	0.958	0.962	0.957	0.963	0.982	0.967
0.2/0.3	0.963	0.964	0.954	0.953	0.977	0.977
0.3/0.4	0.970	0.970	0.940	0.950	0.935	0.942
0.4/0.5	p.921	0.931	0.940	0.946	1.017	1.012
0.5/0.6	0.945	0.945	0.940	0.941	0.902	0.900
0.6/0.7	0.913	0.919	0.933	0.944	0.952	0.943
0.7/0.8	0.944	0.953	0.934	0.937	0.951	0.953

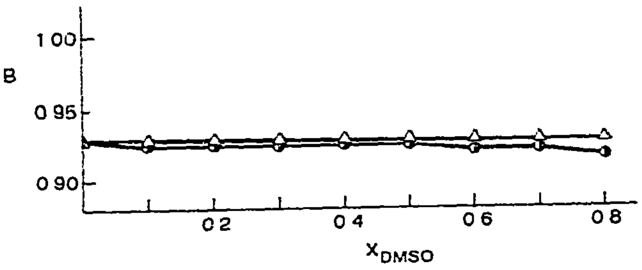

Fig 3. Variation of the *B* parameter values for *p*-chloro- (○), *p*-nitro- (●), and *p*-hydroxybenzoic acid (△) as a function of the mole fraction of DMSO at 25°C.

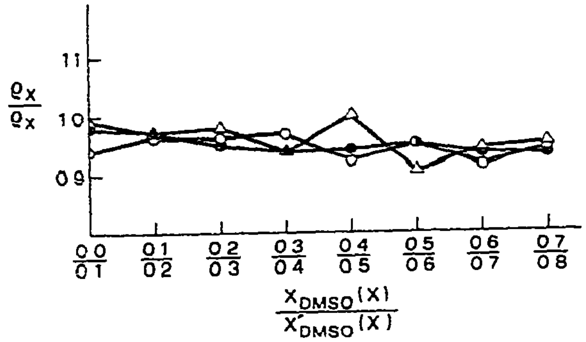

Fig 4. Variation of the $\rho_x/\rho_{x'}$ values for *p*-chloro- (○), *p*-nitro- (●), and *p*-hydroxybenzoic acid (△) as a function of the ratio X_{DMSO}/X'_{DMSO} of the mole fraction of DMSO at 25°C.

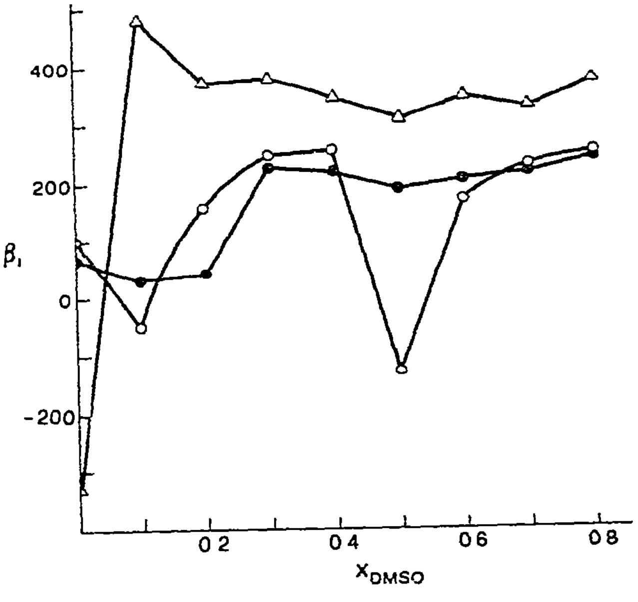

Fig. 5. Variation of the values of the β_1 parameter for *p*-chloro- (○), *p*-nitro- (●), and *p*-hydroxybenzoic acid (△) as a function of the mole fraction of DMSO at 25°C.

TABLE 5

Values of the β_{i} parameter for the ionization of *p*-chloro-, *p*-nitro- and *p*-hydroxybenzoic acid in water–DMSO mixtures at 25°C

X_{DMSO}	*p*-Cl	*p*-NO_2	*p*-OH
0.0	101.19	72.16	−323.8
0.1	−54.44	33.16	479.26
0.2	164.76	58.16	371.16
0.3	245.65	223.00	383.16
0.4	254.64	218.16	339.16
0.5	−136.84	190.22	309.03
0.6	166.2	209.25	348.78
0.7	225.53	219.33	325.56
0.8	253.27	240.93	374.00

deviations reduce to 0.03, 0.03 and 0.04, respectively. This indicates that the *meta*-derivatives [1] approach the experimental values better than the *para*-derivatives. It is also worth noting that the *p*-hydroxy derivative has the largest scattering.

Finally, eqn. (5) can provide the β_{i} values at 298 K in the whole mole fraction range. These values are given in Table 5 and plotted in Fig. 5. Figure 5 shows that the β_{i} parameter values are not constant, this being especially true for the chloro-derivative.

Undoubtedly the presence of the resonance effect in the *para*-derivatives influences the disagreement between experimental results and the thermodynamic model. However, it is impossible to explain the greatest disagreement with the experimental values shown by the chloro-derivative in which the resonance effect is absent.

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