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

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ABSTRACT

Thermodynamic and electrostatic models relating to substituent and solvent effects on organic acids were evaluated. The two models were verified by means of experimental results of *m*-benzoic acid derivatives in water–DMSO solutions. Both the models are consistent with the experimental results in some mole fraction intervals.

INTRODUCTION

Several authors [1–4] have investigated the proton transfer reactions of the type

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

in which PhCOOH is the reference acid (benzoic acid), R–PhCOOH is a derivative of the reference acid, and (s) indicates the solvent in which each species is dissolved. The substituent and solvent effects on such a reaction have been described by means of the Hammett equation which, for the *meta* and *para* derivatives, can be written as

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

For the *ortho* derivatives, the Hammett equation can be modified to [5,6]

$$\delta\Delta G^0 = -2.303RT\rho\sigma + fF + \delta E_s + A \qquad (3)$$

where the fF term is related to inductive and field effects while the δE_s term accounts for the steric effect. Further effects, such as the internal hydrogen bond, can be included in the A term [6].

Hepler [7], in his thermodynamic analysis of substituent and solvent effects, has pointed out the usefulness of expressing thermodynamic functions of reactions of type (1) in terms of "internal" and "environmental"

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contributions as

$$\delta\Delta G^0 = \delta\Delta G_{\text{in}} + \delta\Delta G_{\text{env}}$$

One of the most important relationships in the "internal"–"environmental" theory is

$$\Delta G^0 = \delta\Delta H_{\text{in}}(1+\gamma) \tag{4}$$

in which γ is a solute–solvent interaction parameter which depends on solvent, temperature, pressure and reaction type.

Furthermore, Matsui and Hepler [8] have developed a very interesting electrostatic theory on substituent and solvent effects of organic acids. This electrostatic theory allows calculation of the free energy transfer related to eqn. (1) from a hypothetical solvent with dielectric constant ϵ_i to a real solvent with dielectric constant ϵ_s.

The relation between these two theories gives

$$\delta\Delta G^0 = \delta\Delta H_{\text{in}}\left[1 + \frac{B\epsilon_i}{(1-B)\epsilon_s}\right] \tag{5}$$

and

$$\gamma = B\epsilon_i/(1-B)\epsilon_s \tag{6}$$

where B is a dimensionless solvent-independent parameter.

For a particular reaction series in two solvents with dielectric constants ϵ_x and $\epsilon_{x'}$, it is also possible to write the equation [8]

$$\frac{\rho_x}{\rho_{x'}} = \frac{1 - B\left(\frac{\epsilon_x - \epsilon_i}{\epsilon_x}\right)}{1 - B\left(\frac{\epsilon_{x'} - \epsilon_i}{\epsilon_{x'}}\right)} \tag{7}$$

The experimental results of our previous work are perhaps adequate for testing these models with respect to water–dimethylsulphoxide solutions, with dielectric constants ranging from $\epsilon = 78.54$ (pure water) to $\epsilon = 53.2$ ($X_{\text{DMSO}} = 0.8$).

The experimental values of the ionization of the chloro, nitro and hydroxy *meta* derivatives in water–DMSO solutions may be a good starting point. It is well known that in the *meta* derivatives only the inductive effect is present. But the *m*-hydroxy derivative shows an "anomalous" behaviour owing to the strong interactions with the solvent.

EXPERIMENTAL AND PROCEDURE

The preparation of the DMSO–water mixtures and the technique for obtaining the thermodynamic values for the benzoic acid [9] and the substituted benzoic acids [10–12] have been described previously.

RESULTS AND DISCUSSION

As shown in previous work [13–16], a thermodynamic cycle was used to calculate, in solvent s, a proton transfer process which refers to a gaseous initial thermodynamic state. The values of this term have been assumed as a measure of the "environmental" interactions.

On the other hand, the $\delta\Delta G_{i(g)} = \delta\Delta H_{i(g)}$ values of the transfer proton process in the gaseous phase represent the "internal" interactions [13–15]. Thus, by using eqn. (4), it is possible to calculate the variation of the γ parameter for the *meta* derivatives in the whole mole fraction range. These values are reported in Table 1 and are plotted against DMSO mole fraction in Fig. 1. First, it can be seen that, for the chloro and nitro derivatives, the γ values are very similar and their values decrease as the DMSO content increases. This is consistent with the hypothesis [17–19] that the solute–solvent interactions diminish in the DMSO-rich solutions. Furthermore, it is clear that the influence of the solvent is very strong on the hydroxybenzoic acid, just as expected because of the hydrogen bonding between the hydroxyl group and the solvent molecules. It is interesting to note that the information obtained from the γ values is of more use than that obtained from the ρ values. Furthermore, these findings are in agreement with those obtained by the ρ_s values which, in turn, represent the "external" contributions.

As previously observed [7,17–19], the ρ and γ parameters are functions of the mole fraction. Thus the ρ/γ ratio (see Table 2 and Fig. 2) can be used to give information concerning the relation between these two parameters. The variation of the ρ/γ ratio, as a function of the mole fraction, is nearly identical for the chloro and nitro derivatives. So, for these two derivatives, it seems reasonable to assume the same correlation between the ρ and γ parameters.

TABLE 1

$-\gamma$ Values for the dissociation of the *m*-chloro-, nitro- and hydroxybenzoic acids in water–DMSO mixtures at 25°C

X_{DMSO}	*m*-Cl	*m*-NO_2	*m*-OH
0.0	0.893	0.890	0.868
0.1	0.862	0.864	0.985
0.2	0.844	0.841	1.00
0.3	0.838	0.822	0.985
0.4	0.849	0.800	0.985
0.5	0.768	0.782	0.938
0.6	0.766	0.767	1.062
0.7	0.742	0.750	1.123
0.8	0.706	0.741	1.162

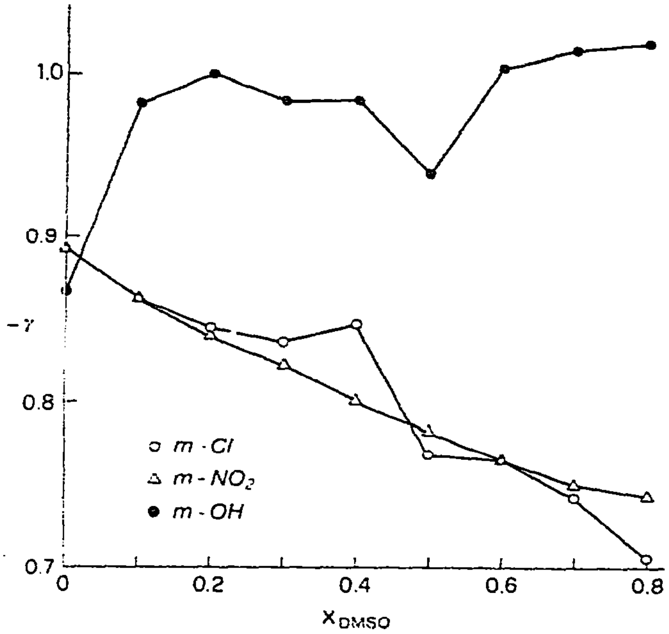

Fig. 1. Variation of the $-\gamma$ values for m-chloro-, nitro- and hydroxybenzoic acids as a function of the mole fraction of DMSO at 25°C.

For the hydroxy derivative, the trend of the ρ/γ ratio is similar but not identical to that of the above-mentioned derivatives. This can be ascribed to better infomation from the γ values on the solvent influence, so that a different connection between the ρ and γ parameters is obtained.

Equation (4) can also be written [7] as

$$\rho\sigma = [C(1+\gamma)/2.303RT][-\delta\Delta H_{\text{in}}/C] \tag{8}$$

where ρ was identified with $[C(1+\gamma)/2.303RT]$ and σ with $[-\delta\Delta H_{\text{in}}/C]$.

TABLE 2

$-\rho/\gamma$ Values for the ionization of the m-chloro-, nitro- and hydoxybenzoic acids in water–DMSO mixtures at 25°C

X_{DMSO}	m-Cl	m-NO$_2$	m-OH
0.0	1.12	1.12	1.15
0.1	1.41	1.40	1.23
0.2	1.60	1.61	1.35
0.3	1.85	1.88	1.57
0.4	1.93	2.00	1.66
0.5	2.28	2.24	1.86
0.6	2.46	2.46	1.80
0.7	2.78	2.75	1.81
0.8	4.10	3.89	2.48

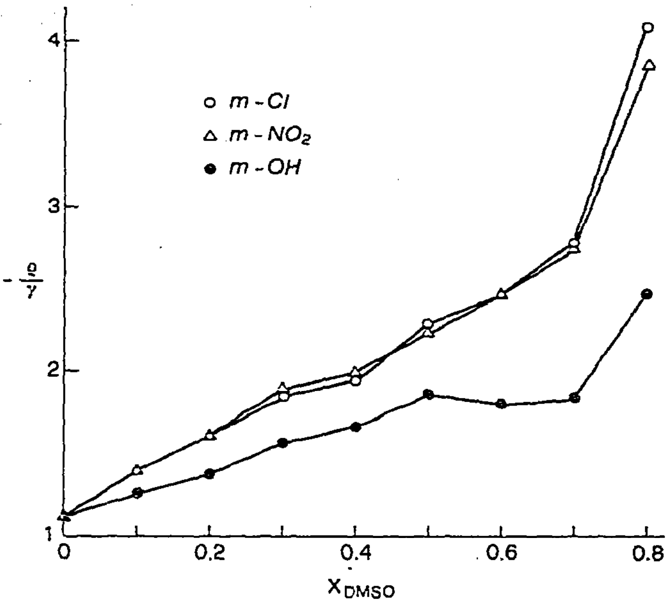

Fig. 2. Variation of the $-\rho/\gamma$ values for *m*-chloro-, nitro- and hydroxybenzoic acids as a function of the mole fraction of DMSO at 25°C.

Using the calculated γ values and the experimental $\delta\Delta H_{\text{in}}$ values [13–15], the C values and thus the σ values have been calculated (see Table 3). The σ values are identical to those previously calculated using the "normal" Hammett equation [17–19]. By including in eqn. (6) γ, ϵ_i [8] and ϵ_s [6] values, it is possible to calculate the values of the B parameter. Values of B for $\epsilon_i = 2.5$ [8] and $\epsilon_i = 6$ [8] have been calculated.

Figure 3 shows that, for $\epsilon_i = 2.5$, the B values are identical for the chloro and nitro derivatives and nearly constant in the various solutions. Again,

TABLE 3

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

X_{DMSO}	*m*-Cl	*m*-NO_2	*m*-OH
0.0	0.369	0.726	0.126
0.1	0.392	0.740	0.012
0.2	0.397	0.775	0.000
0.3	0.360	0.758	0.009
0.4	0.318	0.805	0.009
0.5	0.457	0.822	0.034
0.6	0.427	0.814	−0.031
0.7	0.431	0.799	−0.057
0.8	0.351	0.592	−0.054

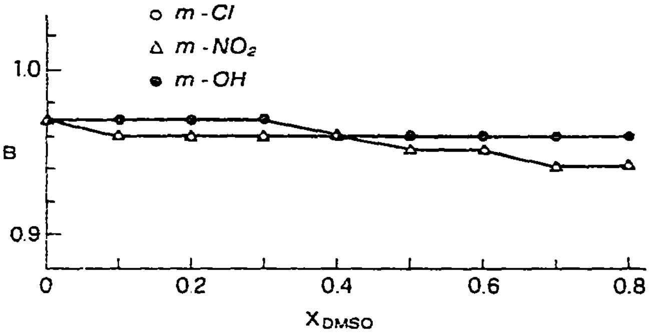

Fig. 3. Variation of the B parameter values for m-chloro-, nitro- and hydroxybenzoic acids as a function of the mole fraction of DMSO at 25°C.

from eqn. (7) it is possible to calculate the variation of the $\rho_x/\rho_{x'}$ ratio in the whole mole fraction range (Table 4 and Fig. 4).

From the difference $|(\rho_x/\rho_{x'})_{calc} - (\rho_x/\rho_{x'})_{exp}|$ between the calculated and experimental [20] ratio, the agreement between our experimental values and the values obtained from eqn. (7) can be determined. For every derivative, the mean and the standard deviation of the differences have been calculated. The best mean and standard deviation for the chloro and nitro derivatives were found assuming $\epsilon_i = 2.5$ while for the hydroxy derivative this is true for $\epsilon_i = 6$.

For the chloro derivative, the mean of the differences is 0.068 and the standard deviation is 0.07. The largest difference is 0.206 at $X_{DMSO} = 0.8$. For the m-nitro derivative, the mean is 0.068, the standard deviation is 0.08 and the largest difference is 0.223 at $X_{DMSO} = 0.8$. Finally, the m-hydroxy derivative shows the values 0.09 for the mean, 0.088 for the standard

TABLE 4

$\rho_x/\rho_{x'}$ Values calculated using eqn. (7) for the dissociation of the m-chloro-, nitro- and hydroxybenzoic acids in water–DMSO mixtures at 25°C

X_{DMSO}/X'_{DMSO}	m-Cl		m-NO$_2$		m-OH	
	$\epsilon_i = 2.5$	$\epsilon_i = 6.0$	$\epsilon_i = 2.5$	$\epsilon_i = 6.0$	$\epsilon_i = 2.5$	$\epsilon_i = 6.0$
0.0/0.1	0.962	0.967	0.976	0.967	1.029	1.040
0.1/0.2	0.958	0.962	0.958	0.962	0.984	0.979
0.2/0.3	0.955	0.959	0.942	0.949	0.951	0.952
0.3/0.4	0.951	0.955	0.940	0.941	0.947	0.953
0.4/0.5	0.908	0.910	0.931	0.943	0.924	0.961
0.5/0.6	0.942	0.947	0.941	0.939	0.944	0.963
0.6/0.7	0.926	0.934	0.927	0.938	0.969	0.968
0.7/0.8	0.920	0.925	0.937	0.934	0.956	0.956

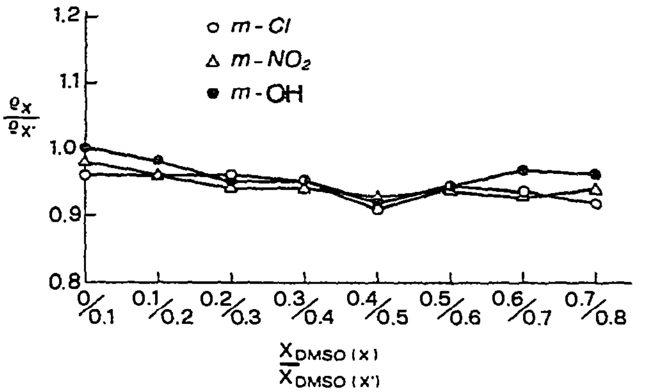

Fig. 4. Variation of the $\rho_x/\rho_{x'}$ values for the *m*-chloro-, nitro- and hydroxybenzoic acids as a function of the ratio $X_{\mathrm{DMSO}}/X'_{\mathrm{DMSO}}$ of the mole fraction of DMSO at 25°C.

deviation and 0.241 for the largest difference. These values show that the chloro derivative approaches the experimental values better than the nitro and hydroxy derivatives. If the first and last ratios are eliminated, it can be seen that the standard deviations of the chloro, nitro and hydroxy derivatives become 0.031, 0.030 and 0.030. It is also worth noting that the scatter of values for the three isomers becomes equal.

From the above evidence, it is apparent that eqn. (7) "works" quite well over the mole fraction range 0.1–0.7. Finally, the relationship between the isoequilibrium temperature parameter β_i and the "environmental" β_e parameter was examined. The equations used are [7]

$$\beta_i = \beta_e - \frac{1+\gamma}{\partial\gamma/\partial T} = T - \frac{1+\gamma}{\partial\gamma/\partial T} \tag{9}$$

and

$$\delta\Delta S^0 = -\delta\Delta H_{in}(\partial\gamma/\partial T) \tag{10}$$

TABLE 5

Values of the β_i parameter for the ionization of the *m*-chloro-, nitro- and hydroxybenzoic acids in water–DMSO mixtures at 25°C

X_{DMSO}	*m*-Cl	*m*-NO_2	*m*-OH
0.0	48.95	75.59	75.02
0.1	−161.81	285.86	292.36
0.2	168.16	237.16	298.16
0.3	208.00	250.16	295.16
0.4	185.00	259.70	286.16
0.5	197.27	258.50	262.16
0.6	229.00	248.59	300.83
0.7	209	230.60	302.43
0.8	240.73	219.68	306.51

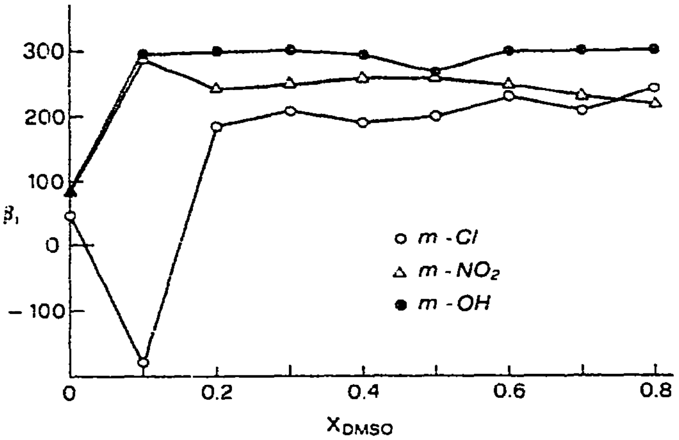

Fig. 5. Variation of the values of the β_i parameter as a function of the mole fraction of DMSO at 25°C.

Including now in eqn. (9) the $\delta\Delta S^0$ [17–19] and $\delta\Delta H_{\mathrm{in}}$ values, the $\partial\gamma/\partial T$ parameter can be calculated. In this way, eqn. (9) can provide the β_i values at 298.16 K for the whole mole fraction range. These values are given in Table 5 and plotted in Fig. 5. Figure 5 shows that for all the isomers the β_i parameter is practically constant from 0.2 to 0.8 mole fraction. In the same mole fraction range, it can be noted that, for the hydroxy derivative, the β_i and β_e parameters are equal, as commonly assumed.

It can be concluded that our experimental values are consistent with the thermodynamic model for solutions having a dielectric constant lower than 74.5 and with the electrostatic model for solutions having a dielectric constant ranging from 77 to 56.7.

The agreement of the experimental results with the thermodynamic model could have been expected by virtue of the absence of the resonance effect in the *meta* derivatives [21]. Further work is now in progress to investigate the consistency of these models with the experimental results of the *para* and *ortho* derivatives.

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