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THERMODYNAMIC STUDY OF THE WATER–DIMETHYLSULFOXIDE SYSTEM. PART II. STUDY OF THE PROTON TRANSFER PROCESSES OF MONOSUBSTITUTED BENZOIC ACIDS, COMPARED WITH THE SAME PROCESSES IN THE GASEOUS PHASE: THERMODYNAMIC AND ELECTROSTATIC MODEL

F. RODANTE

Dipartimento di Ingegneria Chimica dei Materiali, delle Materie Prime e Metallurgia, Università di Roma, via del Castro Laurenziano 7, Roma (Italy)

G. PISTOIA

Centro di Elettrochimica e Chimica Fisica delle Interfasi del C.N.R., via del Castro Laurenziano 7, Roma (Italy)

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ABSTRACT

A thermodynamic study of the water–dimethylsulfoxide system has been carried out.

The thermodynamics of the proton transfer process of monosubstituted benzoic acids, compared with the same processes in the gaseous phase are presented.

The consistency of a thermodynamic and an electrostatic model with the experimental results on some monosubstituted benzoic acids is also reported.

INTRODUCTION

In the first part of this work, a thermodynamic study of the water–dimethylsulfoxide system was presented [1].

The features of the system, thermodynamics of proton transfer processes of monosubstituted benzoic acids, linear free-energy relationships for *meta*, *para* and *ortho* effects are the subject of this paper.

The effect of the medium on the reaction constants was explained in terms of solute–solvent interactions. These were regarded as "external" interactions and were found to be chiefly inductive in character [2–4].

Hepler and co-workers [5–8] proposed the usefulness of expressing thermodynamic functions of reactions of the type

$$(\text{X PhCOOH})_X + (\text{PhCOO}^-)_X = (\text{XPhCOO}^-)_X + (\text{PhCOOH})_X \qquad (1)$$

in terms of "internal" and "external" contributions as in the following

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equations

$$\delta\Delta H^0 = \delta\Delta H_{\text{in}} + \delta\Delta H_{\text{ex}} \tag{2a}$$

$$\delta\Delta S^0 = \delta\Delta S_{\text{in}} + \delta\Delta S_{\text{ex}} \tag{2b}$$

"Internal" effects are those intrinsic to the molecule and the anion of the acid, whereas "external" effects stem from solvent interactions with molecules and anions.

PROTON TRANSFER PROCESSES OF SUBSTITUTED BENZOIC ACIDS COMPARED WITH THE SAME PROCESSES IN THE GASEOUS PHASE

To separate the solvent effects from the intrinsic molecular effects in eqns. (2a) and (2b) it is necessary to know the thermodynamics for the same processes occurring in the gaseous phase.

Information regarding the intrinsic acidities is obtained from the gas-phase proton transfer reactions

$$\mathrm{A_1H + A_2^- = A_1^- + HA_2} \tag{3}$$

The studies were carried out by means of ICR mass spectrometry [9], high-pressure pulsed ion sources [10] and flowing after-glow apparatus measurements [11].

The free-energy changes, ΔG^0, for the proton transfer process in eqn.(3) were determined by measuring $\delta\Delta G^0 = RT \ln K$. The values obtained by McIver and Silvers [12] at 25°C with ICR measurements are in good agreement with those of Yamdagni et al. [13] at 327°C, obtained with high-pressure mass spectrometry.

Furthermore, the entropy terms for such processes in the gaseous phase are assumed to be negligible [13,14] so that $\delta\Delta H_{i(\mathrm{g})} \approx \delta\Delta G^0_{i(\mathrm{g})}$. In some instances, changes of rotational symmetry numbers may lead to a small entropy change which causes a difference of about 1–2 kcal [15] between the enthalpy change and the measured free energy of the reaction. For the same reactions, an uncertainty of the same order of magnitude between $\delta\Delta G^0_{600\ \mathrm{K}}$ and $\delta\Delta G^0_{300\ \mathrm{K}}$ is possible [15].

The cycle used to calculate the "external" interactions employs the benzoic acid as a reference compound as follows

$$\begin{array}{ccccc}
\mathrm{XPhCOOH_{(g)}} & +\mathrm{PhCOO^-_{(g)}} & \delta\Delta \mathrm{P}_{i(\mathrm{g})} & \mathrm{XPhCOO^-_{(g)}} & +\mathrm{PhCOOH_{(g)}} \\
\downarrow \Delta P_{\mathrm{s}} & + \quad \downarrow \Delta P_{\mathrm{s}} & \overset{\rightarrow}{\delta\Delta P}_{i(\mathrm{x})} & \downarrow \Delta P_{\mathrm{s}} & \downarrow \Delta P_{\mathrm{s}} \\
(\mathrm{XPhCOOH})_X & (+\mathrm{PhCOO^-})_X & \rightarrow & (\mathrm{XPhCOO^-})_X & (+\mathrm{PhCOOH})_X
\end{array}$$

So it can be written

$$\begin{aligned}\delta\Delta P_{i(\mathrm{x})} - \delta\Delta P_{i(\mathrm{g})} = {} & [\Delta P_{\mathrm{s}}(\mathrm{XPhCOO^-}) - \Delta P_{\mathrm{s}}(\mathrm{XPhCOOH})] - \\ & [\Delta P_{\mathrm{s}}(\mathrm{PhCOO^-}) - \Delta P_{\mathrm{s}}(\mathrm{PhCOOH})]\end{aligned}$$

and

$$\delta\Delta P_{i(x)} - \delta\Delta P_{i(g)} = \delta\Delta P_s^{g\to x} \tag{4}$$

where $\delta\Delta P_{i(g)}$ will be the gaseous phase change of any thermodynamic property ($P_i = G, H, S$) for the proton transfer from the substituted acid to the benzoic acid. The corresponding value in solvent x is $\delta\Delta P_{i(x)}$.

The right-hand term of eqn. (4) can be assumed as the proton transfer, in solvent x, which refers to a gaseous initial thermodynamic state, i.e., $\delta\Delta P_s^{g\to x} = \delta\Delta P_i^{g\to x}$. Again the $\delta\Delta P_i^{g\to x}$ term is assumed as a measure of the "external" interactions so that it is reasonable to assume that in eqn. (4) the $\delta\Delta P_{i(g)}$ term represents the "internal" interactions, $\delta\Delta P_{i(x)}$ the total interactions and $\delta\Delta P_i^{g\to x}$ the "external" ones.

By using the values of McMahon and Kebarle [14] it is possible to calculate the $\delta\Delta G_{i(g)}$ values of the *m*-, *p*- and *o*-derivatives. The $\delta\Delta G_{i(g)}$ and $\delta\Delta G_{i(x)}$ values [16–22] are included in eqn. (4) and the $\delta\Delta G_i^{g\to x}$ values are calculated. It is wellknown [15] that both the "external" and "internal" rotations in the half-process $HA_1 \rightarrow A_1^-$ occurring in the gaseous phase are responsible for the loss of entropy in eqn. (4) so that $\delta\Delta S_{i(g)} \neq 0$.

However, for reactions such as those considered here, symmetry numbers are small and almost cancel out. Therefore, if $\delta\Delta S_{i(g)}$ is assumed [14] to be equal to zero, then $\delta\Delta G_{i(g)600\ K} \approx \delta\Delta G_{i(g)300\ K} \approx \delta\Delta H_{i(g)300\ K}$, and it is possible to calculate the $\delta\Delta H_i^{g\to x}$ and $T\delta\Delta S_i^{g\to x}$ terms. All these values are reported in Tables 1–3.

These values represent the "external" interactions of the proton transfer of the substituted benzoic acids with the medium. It is interesting to compare the reaction and substituent constant values, previously calculated the (first part of this work [1]) for the proton transfer with the values of the

TABLE 1

Free energy values, $\delta\Delta G_i^{g\to x}$ (kcal mol^{-1}), for the proton transfer process of substituted benzoic acids, in water–DMSO mixtures, calculated by assuming a gaseous initial thermodynamic state

X_{DMSO} =	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
o-Cl	2.08	2.38	2.64	2.63	2.52	2.18	2.41	2.22	2.23
m-Cl	4.20	4.05	3.97	3.94	3.99	3.61	3.60	3.49	3.32
p-Cl	1.54	3.81	3.73	3.76	3.91	3.69	3.69	3.46	3.51
o-NO_2	6.03	6.34	6.48	6.46	6.34	6.17	6.01	5.83	5.68
m-NO_2	8.01	7.78	7.53	7.40	7.20	7.04	6.90	6.75	6.67
p-NO_2	10.07	9.83	9.66	9.49	9.37	9.29	9.14	8.99	8.81
o-OH	11.67	15.23	15.71	10.48	9.99	9.62	9.62	8.91	8.71
m-OH	1.13	1.28	1.30	1.28	1.28	1.12	1.38	1.46	1.51
p-OH	4.52	4.58	4.67	4.93	4.74	5.65	4.97	5.05	5.18
o-CH_3O	0.35	0.66	0.85	0.94	0.91	0.93	1.28	0.99	0.91
p-CH_3O	−0.45	−0.91	−0.34	−0.17	−0.17	−0.80	−0.63	−0.37	−0.19

entropy, $T\delta\Delta S_i^{g\to x}$, and free energy, $\delta\Delta G_i^{g\to x}$, terms. In previous works [2–5], the solute–solvent interactions were expressed as entropy reaction constants.

It was also shown [23] that the shape of the $T\delta\Delta S_i^{g\to x}$ curves for the chloro isomers is very close to that of the entropic reaction constants, ρ_S. Yet the $T\delta\Delta S_i^{g\to x}$ curve gives a measure of the values of the solute–solvent interactions, while ρ_S gives only a trend.

For the nitro isomers it may be noted that in solution the resonance effect appears in the *ortho* anion, while in the gaseous phase this effect occurs for the *para* compound [24].

A comparison with the chloro isomers shows that the transfer process is easier for the nitro isomers in the gas-phase, while the opposite is true in solution [24].

TABLE 2

Enthalpy, $\delta\Delta H_i^{g\to x}$ (kcal mol^{-1}), for the proton transfer process of substituted benzoic acids, in water–DMSO mixtures, calculated by assuming a gaseous initial thermodynamic state

X_{DMSO} =	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
o-Cl	1.20	2.06	5.55	4.64	4.49	4.57	8.22	12.22	9.68
m-Cl	4.63	4.48	5.66	6.57	4.73	6.88	8.36	7.54	10.52
p-Cl	4.55	4.33	5.22	7.51	7.24	4.20	5.30	7.35	9.99
o-NO_2	7.92	8.36	8.46	10.86	11.85	15.89	13.06	13.02	12.21
m-NO_2	9.34	10.62	14.46	17.46	21.19	21.72	22.12	16.64	15.43
p-NO_2	11.43	11.276	11.40	15.88	15.82	14.28	15.73	16.98	20.93
o-OH	13.93	13.61	14.01	14.68	19.02	18.17	18.17	20.59	17.19
m-OH	1.36	2.18	4.46	3.16	7.71	7.89	10.35	12.64	9.03
p-OH	4.27	4.68	7.71	8.26	10.15	11.56	10.71	8.16	9.82
o-CH_3O	0.50	0.91	1.87	3.48	5.50	7.12	9.45	10.11	9.06
p-CH_3O	−0.30	−0.40	−0.57	2.27	4.61	5.90	8.66	−9.03	−6.72

TABLE 3

Values of $T\delta\Delta S_i^{g\to x}$ (kcal mol^{-1}) for the proton transfer process of substituted benzoic acids, in water–DMSO mixtures, calculated by assuming a gaseous initial thermodynamic state

X_{DMSO} =	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
o-Cl	−0.88	−0.32	2.91	1.99	1.97	2.39	5.81	10.01	7.45
m-Cl	0.43	0.43	1.69	2.63	0.74	3.27	4.76	3.75	7.20
p-Cl	3.01	0.52	1.49	3.75	3.33	0.51	1.61	3.89	6.48
o-NO_2	1.89	2.22	1.98	4.40	5.51	9.72	7.06	6.19	6.53
m-NO_2	1.33	2.84	6.93	10.06	13.99	14.68	15.32	9.89	8.76
p-NO_2	1.36	1.44	1.74	6.39	6.45	6.99	6.59	7.99	12.12
o-OH	2.26	−1.61	−1.68	4.20	9.03	8.55	8.55	11.68	8.48
m-OH	−0.25	0.10	3.03	3.33	5.41	5.91	5.77	3.27	4.64
p-OH	0.25	1.00	3.16	1.88	6.43	6.67	8.97	11.18	7.52
o-CH_3O	0.15	0.25	1.02	2.54	4.59	6.19	8.17	9.12	8.15
p-CH_3O	0.15	0.51	0.91	2.38	4.78	6.70	9.29	9.37	6.91

On the behaviour of the hydroxy derivatives it can be noted that since the *o*- and *p*-hydroxybenzoic acids behave, in the gas phase, as phenols, an intramolecular proton transfer process hinders the solvation process [25].

Furthermore, the *ortho* anion solvation is made much more difficult by the internal hydrogen bond.

For the chloro derivative the favourable $\delta\Delta H_{i(g)}$ [23] change in the gas phase, due to an acidifying substituent, is wiped out in solution by an unfavourable effect of the same substituent exerted mostly on the anion. This effect makes the $\delta\Delta H_i^{g\to x}$ change unfavourable over the whole mole fraction range. Keeping as a reference the free-energy transfer process in the gaseous state it is possible to see that, in solution, the free energy exhibits a very limited dependence on the medium effect.

There is also clear evidence that for the *ortho*-derivative the shape of the $\delta\Delta G_i^{g\to x}$ curve is similar to that of the substituent constant, σ_o [23]. Thus, $\delta\Delta G_i^{g\to x}$ values give a measure of the effect of the medium on the structure variation brought about by the substituent group. From the free energy point of view the transfer process is easier in DMSO-rich solutions, this behaviour being similar to that observed in the gas phase.

For the *meta* and *para* chloro derivatives too, the shape of the entropic term $T\delta\Delta S_i^{g\to x}$ is identical to that of the negative entropic reaction constants, with minima at $X_{\mathrm{DMSO}} = 0.4$ and 0.5, respectively [23].

In the DMSO-rich solutions the behaviour is similar to that observed in the gas phase. The $\delta\Delta G_i^{g\to x}$ values also show that the transfer process is easier in the DMSO-rich solutions, although to a lesser extent for the *ortho* derivative.

For the *para* anion, the negative charge is more tightly localized on the carboxylate group, owing to the weaker electron-withdrawing effect of the chloro atom. Therefore, in pure water, the numerous hydrogen bonds decrease the $\delta\Delta G_i^{g\to x}$ value of the *para* derivative with respect the *meta* and *ortho* ones.

Again for the nitro-isomers the curves of the $T\delta\Delta S_i^{g\to x}$ term have shapes very close to those of the reaction constants [24]. It is also interesting to note that the behaviour of the nitro isomers in the gaseous phase is quite different from that observed in solution. Indeed in the former phase the (negative) values of the free energy term related to the transfer process decrease according to the sequence p-$NO_2 > m$-$NO_2 > o$-NO_2. This order can be understood bearing in mind that in the gaseous phase the intramolecular bond is acid-weakening the *ortho*, while the resonance effect is acid-strengthening the *para* isomer. By contrast, in the latter phase the unfavourable effect of the "external" thermodynamic term is in the order m-$NO_2 > p$-$NO_2 > o$-NO_2. It may be noted that for the three isomers the enthalpic term clearly prevails. As previously shown in the mixed solvent the two $-CH_3$ groups of DMSO interfere with the approach of the negative group of the *ortho* anion to the dipole. This allows the *ortho* anion to re-establish the resonance between the phenyl and carboxyl groups. The effective dipole–dipole interactions with the DMSO molecule stabilize the *ortho* anion, thus increasing the acid-strengthening effect.

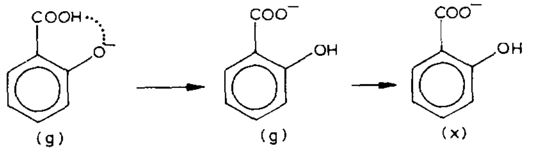
Contrary to what happens in the gas phase, the resonance effect for the *para* anion is very poor, so that the negative charge is mainly localized on the COO^- group where the strongest solvation is observed. Therefore, in solution the resonance effect appears for the *ortho* anion only, while in the gaseous phase the resonance is effective for the *para* isomer.

In solution the *meta* compound shows the least favourable effect to proton transfer. This can be related to the more drastic desolvation of the *meta* anion with respect to the *para* and *ortho* anions.

As previously shown, in the gaseous phase the proton transfer process is easier for the nitro than for the chloro isomers, while in solution the opposite is true. Indeed, in the gas phase the inductive effect of the nitro group is stronger than that of the chloro group. Consequently, in the liquid phase the nitro anions are more desolvated than the chloro anions.

Again, in the gas phase the *o*- and *p*-hydroxy isomers behave as phenols. The greater acidity of the hydroxyl group can be justified by the stabilization of the phenoxide ion, while no equivalent form is available for the *p*-hydroxy benzoate ion [25].

In the liquid phase, the *o*-hydroxybenzoic acid, from the enthalpic point of view, undergoes solvation from the gas phase with more difficulties than the *m*- and *p*-hydroxybenzoic acids. Indeed, the fact that the *ortho* derivative behaves as a phenol allows, in the gas phase, the onset of a strong internal hydrogen bond between the –COOH group and the O^- ion. Thus, in the $\delta\Delta P_s^{g\to x} = \delta\Delta P_i^{g\to x}$ term the intramolecular proton transfer process (I) must be included. Both the intramolecular transfer process and the strong intramolecular hydrogen bond make the $\delta\Delta H_i^{g\to x}$ change unfavourable over the whole mole fraction range. The same intramolecular proton transfer process can be assumed for the *p*-hydroxybenzoic acid. The less unfavourable $\delta\Delta H_i^{g\to x}$ values shown by the *p*-hydroxy compound can be related to the weaker electron-withdrawing effect of the hydroxyl group in the *para* position. It is also interesting to compare the entropic reaction constants, ρ_S, of the proton transfer process with the entropic $T\delta\Delta S_i^{g\to x}$ term. The slope of the $T\delta\Delta S_i^{g\to x}$ curve, for the *p*-hydroxy isomer, is very close (but symmetrical) to that of the entropic reaction constant [25]. This can be related to the negative values of p-σ_{OH} which, in term, also make the ρ_S values negative, by increasing and thus localizing the negative charge of the carboxylate group.



(I)

It can be observed that in the 0.3–0.4 mole fraction range, where p-σ_{OH} values are greatly affected by the solvent composition, the $T\delta\Delta S_i^{g\to x}$ values (this work) are very different from the ρ_S ones [1]. The most favourable $\delta\Delta H_i^{g\to x}$ term for the *m*-hydroxy isomer can be explained with the absence of both the intramolecular transfer process of the intramolecular hydrogen bond and the resonance.

All this contributes to a great localization of charge on the carboxylate group, so that an easier solvation of the anion from the gas phase is possible.

Comparing the nitro-, chloro- and hydroxybenzoic acids the ease of solvation from the gas phase for the *ortho* isomers is in the following order o-Cl > o-NO_2 > o-OH, while for the *meta* isomers, the sequence is: m-Cl > m-OH > m-NO_2, finally, for the *para* isomers it is: p-Cl > p-OH > p-NO_2. It is apparent that with the exception of the *o*-hydroxy isomer the nitro isomers experience the greatest difficulty in undergoing solvation from the gas phase.

This evidence can be further explained by taking into account the "volume" of the nitro group which would show the greatest difficulty in creating a cavity in the medium. Indeed it has to be noted [26] that the radius of the cavity in a solvent is a function of the sum of solvent and solute diameters. Furthermore, while the variation [26] of the free energy of the cavity with the diameter of solvent, for the same molecule of the solute, is very close in water and DMSO, the variation in the enthalpy of the cavity is much greater in DMSO. This is in keeping with our results.

For the methoxy derivatives, the most favourable $\delta\Delta P_i^{g\to x}$ value in the solution from the gas of p-CH_3O with respect to o-CH_3O can be explained with the absence of the intramolecular proton transfer process and of the intramolecular hydrogen bond [21,22].

THERMODYNAMIC AND ELECTROSTATIC MODEL

Some of these acids were used to check a thermodynamic and an electrostatic model related to solvent and substituent effects on the reaction transfer proton processes [27–29].

The first theory allows to calculate the γ and β_i parameters by means of the following equations

$$\delta\Delta G^0 = \delta\Delta H_{in}(1+\gamma) \tag{5}$$

$$\beta_i = \beta_e - \frac{1+\gamma}{\partial\gamma/\partial\tau} \tag{6}$$

where γ is a solute–solvent parameter which depends on the solvent, temperature, pressure and reaction type. γ and β_i values are given in Tables 4 and 5.

Information obtained from the γ parameter is very useful and contributes, along with those from ρ_S and $T\delta\Delta S_i^{g\rightarrow x}$, to the understanding of the solute–solvent interactions related to the proton transfer process of the benzoic acid derivatives in water–DMSO solutions.

β_i is the so-called "isoequilibrium" temperature parameter and is obtained by hypothesising a proportionality between $\delta\Delta H$ and $\delta\Delta S$ values. Furthermore, the requirements for the isoequilibrium relationship are more stringent than those for the free-energy relationship (Hammett equation) which is derived from the former [7,30].

The electrostatic theory allows the calculation of the free energy related to a proton transfer process from a hypothetical solvent with ϵ_i dielectric constant to a real solvent with ϵ_i dielectric constant. In the equation

$$\delta\Delta G^0 = \delta\Delta H\left[1 + \frac{B\epsilon_i}{(1-B)\epsilon_j}\right] \tag{7}$$

TABLE 4

– γ values for the dissociation of some benzoic acids in water–DMSO mixtures at 25°C

X_{DMSO}	m-Cl	m-NO_2	m-OH	p-Cl	p-NO_2	p-OH	o-Cl	o-NO_2	o-OH
0.0	0.893	0.890	0.868	0.935	0.907	1.130	0.550	0.690	0.880
0.1	0.862	0.864	0.985	0.866	0.886	1.145	0.630	0.720	0.860
0.2	0.844	0.841	1.000	0.848	0.870	1.168	0.690	0.740	0.820
0.3	0.838	0.822	0.985	0.854	0.855	1.243	0.700	0.730	0.790
0.4	0.849	0.800	0.985	0.889	0.844	1.185	0.660	0.720	0.750
0.5	0.768	0.782	0.983	0.839	0.837	1.413	0.570	0.700	0.720
0.6	0.766	0.767	1.062	0.839	0.823	1.243	0.630	0.680	0.690
0.7	0.742	0.750	1.123	0.785	0.820	1.263	0.580	0.660	0.670
0.8	0.706	0.741	1.162	0.798	0.793	1.295	0.590	0.650	0.650

TABLE 5

Values of the β_i parameter for the ionization of some benzoic acids in water–DMSO mixtures at 25°C

X_{DMSO}	m-Cl	m-NO_2	m-OH	p-Cl	p-NO_2	p-OH	o-Cl	o-NO_2	o-OH
0.0	48.95	75.59	75.02	101.19	72.16	−323.8	11.26	1.66	228.99
0.1	−161.81	285.86	292.36	−54.44	33.16	479.26	48.26	−57.03	268.16
0.2	168.16	237.16	298.16	164.76	58.16	371.16	−95.41	−95.41	292.90
0.3	208.00	250.16	295.16	245.64	223.00	383.16	−160.37	−150.64	314.31
0.4	185.00	259.70	286.16	254.64	218.16	339.16	−184.41	−175.64	97.23
0.5	197.27	258.5	262.26	−136.84	190.22	309.03	−219.84	−220.81	418.15
0.6	229.00	248.59	300.00	166.2	209.25	348.78	−183.84	−256.6	907.69
0.7	209	230.60	302.43	225.53	219.33	325.56	−302.84	−299.44	607.04
0.8	240.73	219.68	306.51	253.27	240.93	374.00	−342.84	−374.14	822.54

B is a dimensionless solvent-independent parameter. Furthermore, it is possible to write

$$\frac{\rho_x}{\rho'_x} = \frac{1 - B(\epsilon_x - \epsilon_i/\epsilon_x)}{1 - B(\epsilon'_x - \epsilon'_i/\epsilon'_x)} \tag{8}$$

where ρ_x and ρ'_x are the reaction constant of a given reaction, in two solvents of dielectric constant ϵ_x and ϵ'_x, respectively.

While the electrostatic model is consistent with the experimental values of all isomers considered (with the exception of the *ortho*-chloro derivative) for the thermodynamic model, this is true for the *meta* derivatives only [27–29]. This confirms the idea that the requirements for an isoequilibrium relationship are more stringent than those for a free-energy relationship.

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 hydroxyl 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.

For the hydroxy derivative it is also interesting to note that the γ values are very close to those of the $T\delta\Delta S_i^{g\to x}$ entropy term and very different from the ρ_S term [27]. This confirms that the information obtained from the γ values is more useful than that obtained from the ρ_S values.

Equation (5) can also be written as

$$\rho\sigma = [C(1+\gamma)/2.303RT][\delta\Delta H_{in}/C] \tag{9}$$

Using the calculated γ values and the experimental $-\delta\Delta H_{in}$ values, the C values and thus the σ values have been calculated. The σ values are identical to those previously calculated using the "normal" Hammett equation (Table 6). In eqn. (9), ρ was related to $C(1+\gamma)/2.303RT$ and σ to $-\delta\Delta H_{in}/C$ [27–29].

TABLE 6

σ_m, σ_p and σ_o values calculated using the equation $\sigma = -\delta\Delta H_{in}/C$ in water–DMSO mixtures at 25°C

X_{DMSO}	*m*-Cl	*m*-NO$_2$	*m*-OH	*p*-Cl	*p*-NO$_2$	*p*-OH	*o*-Cl	*o*-NO$_2$	*o*-OH
0.0	0.369	0.726	0.126	0.210	0.757	0.381	0.295	0.650	−0.436
0.1	0.392	0.740	0.012	0.356	0.765	0.350	0.427	0.786	−0.571
0.2	0.397	0.775	0.000	0.362	0.781	0.364	0.388	0.868	−0.031
0.3	0.360	0.758	0.009	0.304	0.761	0.450	0.344	0.777	0.080
0.4	0.318	0.804	0.009	0.218	0.775	0.331	0.384	0.796	0.270
0.5	0.457	0.822	0.034	0.218	0.758	0.691	0.508	0.816	0.148
0.6	0.427	0.814	−0.031	0.275	0.763	0.377	0.368	0.808	0.430
0.7	0.431	0.799	−0.057	0.336	0.749	0.374	0.411	0.808	0.503
0.8	0.351	0.592	−0.054	0.220	0.581	0.299	0.363	0.780	0.580

For the *para* derivatives [28] there is also a good agreement between ρ_S and γ values with the exception of *p*-OH, this being due to the resonance effect which mostly occurs in the 0.45–0.55 mole fraction range. Again the γ_{OH} values are similar to the $T\delta\Delta S_i^{g\to x}$ values. The substituent reaction constant calculated by means of $\sigma = -\delta\Delta H_{in}/C$ are very close to that calculated by means of the "normal" Hammett equation (Table 6). For the *ortho* derivatives the γ values are very different from each other, but their values are very useful and contribute, along with those from ρ_S and $T\delta\Delta S_i^{g\to x}$, to a more exact picture of the solute–solvent interactions [29].

The differences $(\rho_x/\rho_x')_{calc} - (\rho_x/\rho_x')_{exp}$ between the calculated and the experimental ratios can be obtained by means of eqn. (8). The *meta* and *para* derivatives approach the experimental values better than the *ortho* derivatives. It is worth noting that in this case the *ortho*-chloro derivative has the largest scattering [27–29]. Thus, it may be stressed that the inductive effect of the chlorine atom plays a very important role in the so-called "*ortho* effect".

Finally, eqn. (6) can provide the "isoequilibrium" temperature parameter, β_i.

For the *meta* derivatives the experimental values are consistent with the thermodynamic model. This could have been expected by virtue of the absence of the resonance effect in the *meta* derivatives [27].

For the *para*-derivatives it can be shown that the β_i values do not tend to be constant, this being especially true for the chloro derivatives.

Undoubtedly the presence of the resonance effect in the *para* derivatives influences the disagreement between the experimental results and the thermodynamic model. However, it is impossible to explain the great disagreement with the experimental values shown by the chloro derivatives in which the resonance is absent [28].

Finally, none of the three *ortho* isomers show any agreement between experimental results and the thermodynamic model. This could have been expected from the occurrence of the resonance, field and steric effects [29]. It can be noted that while the electrostatic model is consistent with the experimental values of all isomers considered (with the exception of the *ortho*-chloro derivative), for the thermodynamic model, this is true for the *meta* derivative only. It can be concluded that in this study the values obtained from "external" interactions, $\delta\Delta P_i^{g\to x}$, together with those of the γ parameter, give further and more useful information on the solute–solvent interactions.

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