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STATISTICAL STUDY OF THE INFLUENCE OF THE HYDROXYL GROUPS IN POSITIONS 3 AND 4 ON THE IONIZATION PROCESS OF 3,4-DIHYDROXYBENZOIC ACID

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ABSTRACT

The contributions of each of the two hydroxyl groups to the ionization and solvation processes for 3,4-dihydroxybenzoic acid were studied by considering the enthalpy values of these processes as a linear combination of those related to the same processes for the 2,3-dihydroxy and 2,4-dihydroxy derivatives in water–dimethylsulphoxide mixtures with the mole fraction of dimethylsulphoxide ranging from 0 to 0.8. For this purpose, diparametric and monoparametric regression analyses were used. In these analyses, the total standard deviations, slope and intercept standard deviations, correlation coefficients, null hypotheses $a = 0$, $b = 0$, $r = 0$ (where a is the intercept, b the slope and r the regression coefficient), the Student t test and F test of the above cited values were taken into account.

Particular attention was paid to the presence of the so-called collinearity between the explanatory variables.

The introduction of a hydroxyl group in position 3 destabilizes the benzene ring, overcoming the stabilization effect caused by the hydroxyl in position 4.

INTRODUCTION

The influence of the hydroxyl groups on the ionization processes for the series of monohydroxy- and dihydroxy-substituted benzoic acids as a function of the solvation of the respective ions and undissociated molecules has been systematically studied in our laboratory [1–7]. It was found that the driving forces of the ionization processes for the monohydroxy- and dihydroxy-substituted series are the solvation of the ions and the solvation of the undissociated molecules respectively. Water–dimethylsulphoxide (DMSO) solutions provide an effective system for studying the solvation energies. Indeed, water has always been considered a suitable solvent for many

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reactions, DMSO, in turn, has many uses as a medium for chemical reactions [8] owing to its powerful solvation ability for various organic and inorganic compounds. Obviously, in the disubstituted series, the interactions between the two groups play the principal role in the solvation of the molecules.

It is also noteworthy that in the dihydroxy-substituted series studied previously, there is always a hydroxyl group in position 2, the other hydroxyl being in position 3 or 4 or 5 or 6.

This work aims to study the reciprocal influence of the two hydroxyls in positions 3 and 4 and to explain this effect by means of a comparison with those of the previously studied dihydroxy derivatives.

Such a comparison is common practice in organic chemical physics, where, for example, small variations in structure can take place in the skeleton of a molecule, owing to the introduction of different groups in the same positions or of the same groups in different positions.

It is also well known that in statistical analysis the linear monoparametric and diparametric equations are able to supply useful methods for comparing and explaining the experimental results in terms of the probability [9–14] of the above-cited structure variations. However, there is a distinct possibility of using the results obtained incorrectly, this resulting in misleading conclusions. Especially for the diparametric linear regression, particular attention must be paid to the so-called collinearity, i.e. the presence of correlations between one independent (explanatory) variable and another. In this context, more useful tests are standard deviations of the slope and of the intercept, the total standard deviation, the Student t test and the F test for the intercept, slope and correlation coefficient values of the monoparametric and diparametric regressions.

EXPERIMENTAL DETAILS AND PROCEDURE

The calorimetric measurements were performed with a Tronac 450 calorimeter and an L.K.B. 8700 reaction and solution calorimeter.

The calorimetric measurements were read by means of a BASIC program which was run on an Olivetti M24 computer [15].

DMSO (Erba, RP) was purified according to the procedure of Synnot and Butler [16]. Water–DMSO mixtures were prepared by weighing purified DMSO and CO_2-free, twice-distilled water. The mole fraction of DMSO in these mixtures ranged from 0.0 to 0.8. An aqueous solution of 0.099 M NaOH and solutions of 0.99 M HCl in various water–DMSO mixtures were prepared from standard solutions and their concentrations were checked by potentiometric titrations. 3,4-Dihydroxybenzoic acid ($3,4(OH)_2PhCOOH$) (Fluka) was purified by crystallization from water–ether mixtures and its melting point checked before use.

Solutions of the sodium salt 3,4-$(OH)_2$PhCOONa) were prepared by adding an NaOH solution of known molarity to 3,4-$(OH)_2$PhCOOH dissolved in the water–DMSO mixtures. As a result, 100g of water–DMSO solution of X mole fraction of DMSO were obtained. The concentration of the sodium salt was always in the range (2–4) $\times 10^{-3}$ M.

A certain amount of acid (about 4%–5% of the original content) was not converted into the salt and remained as free acid to avoid the presence of free alkali. The ionization process of 2,3-dihydroxybenzoic acid (3,4-$(OH)_2$PhCOOH) in the various water–DMSO mixtures of X mole fraction DMSO can be represented as

$$[3,4\text{-}(OH)_2PhCOOH]_X \rightarrow [3,4\text{-}(OH)_2PhCOO^-]_X + (H^+)_X \tag{1}$$

The partial molar enthalpy of ionization $\Delta\overline{H}_1$ of 3,4-$(OH)_2$PhCOOH acid was obtained by experimental measurements of: (a) Partial molar enthalpy of reaction $\Delta\overline{H}_2$ of 3,4-$(OH)_2$PhCOONa dissolved in the mixed solvent of X mole fraction DMSO, with 0.99 M HCl also dissolved in the solvent of X mole fraction DMSO:

$$\begin{aligned}&[3,4\text{-}(OH)_2PhCOO^-]_X + (Na^+)_X + (H^+)_X + (Cl^-)_X\\&\quad = [3,4\text{-}(OH)_2PhCOOH]_X + (Na^+)_X + (Cl^-)_X\end{aligned} \tag{2}$$

(b) The partial molar enthalpy of dilution $\Delta\overline{H}_3$ of the same amount of 0.99 M HCl (dissolved in X mole fraction DMSO):

$$(H^+)_X + (Cl^-)_X = (H^+)_X + (Cl^-)_X \tag{3}$$

The partial molar enthalpy of process (1) can be obtained by subtracting $\Delta\overline{H}_2$ from $\Delta\overline{H}_3$. For each of the water–DMSO mixtures at X mole fraction DMSO, the $\Delta\overline{H}_1$ refers to the ionization process of 1 mol of 3,4-$(OH)_2$PhCOOH dissolved at infinite dilution in 1000 g of mixed solvent, yielding 1 mol of protons and 1 mol of 3,4-$(OH)_2PhCOO^-$ ions solvated in the same amount of solvent.

In order to refer process (1) to an initial thermodynamic state only, the solution enthalpies of crystalline 3,4-$(OH)_2$PhCOOH. $\Delta\overline{H}_s$, in the various solvent mixtures were measured:

$$3,4\text{-}(OH)_2PhCOOH_{(cry)} \rightarrow [3,4\text{-}(OH)_2PhCOOH]_X \tag{4}$$

so that $\Delta\overline{H}_5 = \Delta\overline{H}_4 + \Delta\overline{H}_1$ values obtained for the process

$$3,4\text{-}(OH)_2PhCOOH_{(cry)} \rightarrow [3,4\text{-}(OH)_2PhCOO^-]_X + (H^+)_X \tag{5}$$

refer to an identical initial thermodynamic state. In processes (2) and (4) concentrations ranging from 2×10^{-3} to 4×10^{-3} M were used. Therefore, the $\Delta\overline{H}$ values related to these processes were assumed to be equal to the ΔH^0 values [17].

A program which supplies monoparametric and diparametric linear regression equations, with a total standard deviation, slope and intercept standard deviations and correlation coefficients for all the above values, was run on an Olivetti M 24 computer.

Moreover, for the monoparametric regression equation $Y = a + bx$ (where a is the intercept and b the slope of the equation) the following null hypotheses were considered: (1) for the intercept, $a = 0$; (2) for the slope, $b = 0$; (3) for the correlation coefficient, $r = 0$. The null hypotheses were tested by using the Student t test. The t values of a, b and r were calculated by means of the expressions

$$t_a = (a - A)/S_a$$

$$t_b = (b - B)/S_b$$

$$t_r = |r|\left[(n-2)/1 - r^2\right]^{1/2}$$

where $A = 0$, $B = 0$ and S_a and S_b are the standard deviations of a and b, and they were compared with those of a set of t tables. If $t > t_{\mathrm{CL},n-2}$ where $n - 2$ is the degree of freedom and CL the confidence level for the significance of the regression, then for $\mathrm{CL} < 0.95$ the null hypothesis is accepted (chemical hypothesis) while for $\mathrm{CL} > 0.999$ its rejection is highly significant. The closeness of the diparametric fit was tested by means of an F test. The F values were calculated from the expressions $F = r^2(n-3)/2(1-r^2)$ and were compared with those of $F_{\mathrm{CL},2,n-3}$ tables where $n - 3$ is the degree of freedom and CL is the confidence level.

If $F > F_{\mathrm{CL},2,n-3}$ at $\mathrm{CL} > 0.999$, then the closeness of the fit is highly significant.

Moreover, for the diparametric regression $Y = a + b_1X_1 + b_2X_2$, a comparison between parameters b_1 and b_2, after their "standardization" [9,14] by means of the equations

$$b_1' = |b_1|\left[\Sigma(X_1 - \bar{X}_1)^2/\Sigma(Y - \bar{Y})^2\right]^{1/2}$$

$$b_2' = |b_2|\left[\Sigma(X_2 - \bar{X}_2)^2/\Sigma(Y - \bar{Y})^2\right]^{1/2}$$

allows the percentage of correlation between X_1 or X_2 with Y to be calculated.

The effect of collinearity is to increase the standard errors of the regression coefficients b_1 and b_2.

RESULTS AND DISCUSSION

Table 1 shows ΔH^0 values of processes (1), (4) and (5).

For the sake of comparison, it is convenient to express the value of the ionization enthalpy ΔH_1^0 as the difference between the values obtained in the mixed solvent at X mole fraction DMSO and those in pure water, so that

$$\delta\Delta H_1^0 = (\Delta H_1^0)_X - (\Delta H_1^0)_{X=0}$$

TABLE 1

Enthalpy values (kcal mol^{-1}) of processes (1), (4) and (5) for the 3,4-dihydroxybenzoic acid in water–DMSO mixtures of various molar fractions (X) of DMSO at 25 °C

X(DMSO)	ΔH_1^0	ΔH_4^0	ΔH_5^0
0.0	0.54	6.75	7.29
0.1	1.13	6.33	7.46
0.2	1.37	4.44	5.81
0.3	2.69	2.04	4.73
0.4	3.62	−0.35	3.27
0.5	4.31	−1.77	2.54
0.6	5.32	−2.79	2.53
0.7	6.85	−3.35	3.50
0.8	9.51	−3.77	5.73

These values are relative to the transfer of the ionization process, while the $\delta\Delta H_4^0$ and $\delta\Delta H_5^0$ values represent the transfer enthalpy of the undissociated molecules and of the two ions H^+ and 3,5-$(OH)_2PhCOO^-$ respectively from pure water to mixed solvent.

All these data are given in Table 2. As for the other dihydroxy derivatives [1,5–8], the $\delta\Delta H_1^0$ term is not favourable to process (1), owing to the greater solvation of the undissociated molecule with respect to the anion.

A calorimetric acidity scale could be useful for understanding the different effects of the hydroxyl groups at the different positions in the benzene ring. The order based on the ionization enthalpies (Table 3) is 2,6-$(OH)_2PhCOOH$ > 2,5-$(OH)_2PhCOOH$ > 2,4-$(OH)_2PhCOOH$ > 2,3-$(OH)_2$-$PhCOOH$ > 3,4-$(OH)_2$-$PhCOOH$. The 3,4-dihydroxy derivative is the weakest acid. This can be explained by taking into account the solvation values of the ions and of the undissociated molecules of all the dihydroxy derivatives (Tables 4 and 5). From these values, the following scale of solvation for the ions can be inferred: 2,6-$(OH)_2PhCOO^-$ > 2,5-

TABLE 2

Enthalpy for the transfer of the ionization ($\delta\Delta H_1^0$), transfer enthalpies of the undissociated molecules ($\delta\Delta H_4^0$) and of the ions ($\delta\Delta H_5^0$) of the 3,4-dihydroxybenzoic acid from pure water to solvent mixtures

X(DMSO)	$\delta\Delta H_1^0$	$\delta\Delta H_4^0$	$\delta\Delta H_5^0$
0.1	0.59	−0.42	−0.17
0.2	0.83	−2.31	−1.48
0.3	2.15	−4.71	−2.59
0.4	3.08	−7.10	−4.02
0.5	3.77	−8.52	−4.75
0.6	4.78	−9.54	−4.76
0.7	6.31	−10.10	−3.79
0.8	8.81	−10.12	−1.56

TABLE 3

Ionization values (kcal mol^{-1}) for some dihydroxybenzoic acids in various water–DMSO mixtures at 25 °C

X(DMSO)	2,6-$(OH)_2$-PhCOOH	2,5-$(OH)_2$-PhCOOH	2,4-$(OH)_2$-PhCOOH	2,3-$(OH)_2$-PhCOOH	3,4-$(OH)_2$-PhCOOH
0.0	0.14	0.39	0.45	0.57	0.54
0.1	0.04	0.59	0.74	0.23	1.13
0.2	−0.03	0.67	0.87	0.48	1.37
0.3	−0.01	0.71	0.71	0.69	2.69
0.4	−0.06	0.75	1.19	1.17	3.62
0.5	−0.03	0.97	1.87	1.74	4.31
0.6	0.03	1.56	2.77	2.55	5.32
0.7	0.12	2.27	3.20	2.63	6.85
0.8	0.23	2.94	3.95	4.29	9.51

TABLE 4

Solvation enthalpies (kcal mol^{-1}) for the ions of some dihydroxybenzoic acids in water–DMSO mixtures at 25 °C

X(DMSO)	2,6-$(OH)_2$-PhCOOH	2,5-$(OH)_2$-PhCOOH	2,4-$(OH)_2$-PhCOOH	2,3-$(OH)_2$-PhCOOH	3,4-$(OH)_2$-PhCOOH
0.1	0.15	0.17	0.17	−0.59	−0.17
0.2	−1.14	−1.20	−1.38	−1.53	−1.48
0.3	−3.92	−3.63	−4.08	−3.48	−2.56
0.4	−5.84	−5.67	−5.74	−5.02	−4.02
0.5	−7.03	−6.90	−6.62	−5.79	−4.75
0.6	−7.59	−7.19	−6.77	−6.01	−4.76
0.7	−5.58	−7.03	−6.93	−5.71	−3.79
0.8	−7.54	−6.86	−6.58	−5.34	−1.56

TABLE 5

Solvation enthalpies (kcal mol^{-1}) for the undissociated molecules of some dihydroxybenzoic acids in water–DMSO mixtures at 25 °C

X(DMSO)	3,4-$(OH)_2$-PhCOOH	2,4-$(OH)_2$-PhCOOH	2,5-$(OH)_2$-PhCOOH	2,3-$(OH)_2$-PhCOOH	2,6-$(OH)_2$-PhCOOH
0.1	−0.42	−0.12	−0.03	−0.25	0.25
0.2	−2.31	−1.80	−1.48	−1.44	−0.86
0.3	−4.71	−4.34	−3.95	−3.60	−3.61
0.4	−7.10	−6.48	−6.03	−5.62	−5.53
0.5	−8.52	−8.04	−7.48	−6.96	−6.75
0.6	−9.54	−9.09	−8.36	−7.99	−7.37
0.7	−10.10	−9.68	−8.91	−8.77	−7.45
0.8	−10.52	−10.08	−9.41	−9.06	−7.52

$(OH)_2PhCOO^- > 2{,}4\text{-}(OH)_2PhCOO^- > 2{,}3\text{-}(OH)_2PhCOO^- > 3{,}4\text{-}(OH)_2PhCOO^-$. For the undissociated molecules the scale of solvation shows the following order: $3{,}4\text{-}(OH)_2PhCOOH > 2{,}4\text{-}(OH)_2PhCOOH > 2{,}5\text{-}(OH)_2PhCOOH > 2{,}3\text{-}(OH)_2PhCOOH > 2{,}6\text{-}(OH)_2PhCOOH$. The fact that $3{,}4\text{-}(OH)_2PhCOOH$ is the weakest acid over the whole mole fraction range, $\Delta X_{DMSO} = 0\text{–}0.8$, is apparently related to the small solvation of the anions and to the large solvation of the undissociated molecule.

In order to understand better the contribution of each of the two hydroxyl groups to the ionization and solvation processes for the 3,4-dihydroxy compound, it is possible to consider the enthalpy values of these processes as a linear combination of those related to the same processes occurring for the 2,3-dihydroxy and 2,4-dihydroxy derivatives over the whole mole fraction range. Indeed, both compounds bear a hydroxyl in the same position, (position 2), the second being in the positions 3 and 4 respectively.

Using a linear diparametric regression between the enthalpy values of the 3,4-dihydroxy, 2,4-dihydroxy and 2,3-dihydroxy derivatives for the ionization and solvation processes we obtain the equation

$$Y = a + b_1X_1 + b_2X_2$$

where $Y = \Delta H_{3,4}$, $X_1 = \Delta H_{2,3}$ and $X_2 = \Delta H_{2,4}$, a is the intercept and b_1 and b_2 the slopes.

The diparametric equation, together with the two corresponding monoparametric equations and the collinearity regression can give a more complete picture of the contributions of hydroxyl groups in positions 3 and 4 in the above-cited processes.

Ionization processes

The values obtained for the diparametric regression equation are given in Table 6. The large value of the standard deviation for $\Delta H_{2,4}$ is due, as previously shown, to the high degree of association between the independent variables $\Delta H_{2,3}$ and $\Delta H_{2,4}$. The high degree of association is measured by the high significance of the monoparametric linear regression between $\Delta H_{2,3}$ and $\Delta H_{2,4}$ (Table 7). Thus the contributions of $2{,}3\text{-}(OH)_2PhCOOH$ and $2{,}4\text{-}(OH)_2PhCOOH$ to the ionization process of $3{,}4\text{-}(OH)_2PhCOOH$ cannot be compared.

Solvation processes of undissociated molecules

The diparametric regression equation related to the solvation processes of the undissociated molecules shows that the standard deviation of the slope of $\Delta H_{2,3}$ is sufficiently large to rule out this term (Table 8). The high significance of linear regression equation between $\Delta H_{2,3}$ and $\Delta H_{2,4}$ confirms that there is high collinearity between the independent variables (Table 9). The $\Delta H_{3,4}$ vs. $\Delta H_{2,3}$ correlation is significant, while $\Delta H_{3,4}$ vs. $\Delta H_{2,4}$ is

TABLE 6

Results of diparametric regression analysis of the ionization process for 3,4-dihydroxybenzoic acid as a function of the 2,3- and 2,4-dihydroxy derivative ionization processes

n [a]	9
a	0.29
b_1	1.41
b_2	0.79
SD(a)	0.45
SD(b_1)	0.83
SD(b_2)	0.88
SD of regression	0.69
r [c]	0.98
F	72.75 [d]

[a] n, number of points.
[b] SD, standard deviation.
[c] r, correlation coefficient.
[d] $F > F_{CL,2,n-3}$ at CL > 0.999, where CL is confidence level.

highly significant (Table 9). Once again it is not possible to compare the influence of $\Delta H_{2,3}$ and $\Delta H_{2,4}$ on the $\Delta H_{3,4}$ values.

Solvation processes of ions

The diparametric regression relative to ion solvation indicates that in this case the values of coefficients b_1 and b_2 (both large with respect to their standard deviations) are comparable (Table 10). The "standardized" coefficients b_1' and b_2' represent 67.74% and 32.26% of the influence of $\Delta H_{2,3}$ and $\Delta H_{2,4}$ respectively on the $\Delta H_{3,4}$. Accordingly, the regression between $\Delta H_{3,4}$ and $\Delta H_{2,3}$ is significant, while that between $\Delta H_{3,4}$ and $\Delta H_{2,4}$ shows an uncertain significance (i.e. there is not collinearity) (Table 11).

TABLE 7

Results of monoparametric regression analysis of the ionization process for 3,4-dihydroxybenzoic acid as a function of the 2,3- and 2,4-dihydroxy derivative ionization processes

	$\Delta H_{2,3}$ vs. $\Delta H_{2,4}$	$\Delta H_{3,4}$ vs. $\Delta H_{2,3}$	$\Delta H_{3,4}$ vs. $\Delta H_{2,4}$
n	9	9	9
Intercept	−0.21	0.52	−0.01
Slope	1.03	2.14	2.25
SD of intercept	0.19	0.37	0.46
SD of slope	0.09	0.18	0.22
SD of regression	0.31	0.68	0.78
r	0.97	0.98	0.97
nh [a]: intercept = 0	CL < 0.95	CL < 0.95	CL < 0.95
nh: slope = 0	CL > 0.999	CL > 0.999	CL > 0.999
nh: $r = 0$	CL > 0.999	CL > 0.999	CL > 0.999

[a] nh, null hypothesis.

TABLE 8

Results of diparametric regression analysis of the undissociated molecule solvation process for 3,4-dihydroxybenzoic acid as a function of the 2,3- and 2,4-dihydroxy derivative molecule solvation processes

n	8
a	−0.38
b_1	−0.27
b_2	1.25
SD(a)	0.70
SD(b_1)	0.21
SD(b_2)	0.19
SD of regression	0.93
r	1.00
F	132.12 [a]

[a] $F > F_{\mathrm{CL},2,n-3}$ at CL > 0.999.

TABLE 9

Results of the monoparametric regression analysis of the undissociated molecule solvation process for 3,4-dihydroxybenzoic acid as a function of the 2,3- and 2,4-dihydroxy derivative molecule solvation processes

	$\Delta H_{2,3}$ vs. $\Delta H_{2,4}$	$\Delta H_{3,4}$ vs. $\Delta H_{2,3}$	$\Delta H_{3,1}$ vs. $\Delta H_{2,4}$
n	8	8	8
Intercept	0.093	−0.52	−0.47
Slope	0.89	1.12	0.99
SD of intercept	0.12	0.18	0.15
SD of slope	0.01	0.03	0.02
SD of regression	0.18	0.26	0.21
r	1.00	0.997	0.998
nh: intercept = 0	CL < 0.95	0.35 < CL < 0.99	0.95 < CL < 0.99
nh: slope = 0	CL > 0.999	CL > 0.999	CL > 0.999
nh: $r = 0$	CL > 0.999	0.99 < CL < 0.999	CL > 0.999

TABLE 10

Results of the diparametric regression analysis of the ion solvation process for 3,4-dihydroxybenzoic acid as a function of the 2,3- and 2,4-dihydroxy derivative ion solvation processes

n	8
a	1.57
b_1	3.63
b_2	−2.26
SD(a)	1.16
SD(b_1)	1.68
SD(b_2)	1.28
SD of regression	0.86
r	0.91
F	12.04 [a]

[a] $F > F_{\mathrm{CL},2,n-3}$ at 0.99 < CL < 0.999.

TABLE 11

Results of the monoparametric regression analysis of the ion solvation process for 3,4-dihydroxybenzoic acid as a function of the 2,3- and 2,4-dihydroxy derivative ion solvation processes

	$\Delta H_{3,4}$ vs. $\Delta H_{2,3}$	$\Delta H_{3,4}$ vs. $\Delta H_{2,4}$
n	8	8
Intercept	−0.47	−0.52
Slope	0.59	0.50
SD of intercept	0.72	0.82
SD of slope	0.15	0.15
SD of regression	0.99	1.10
r	0.84	0.80
nh: intercept = 0	CL < 0.95	CL < 0.95
nh: slope = 0	0.99 < CL < 0.999	0.95 < CL < 0.99
nh: $r = 0$	0.99 < CL < 0.999	0.95 < CL < 0.99

It can thus be noted that the ion desolvation, due to the hydroxyl in position 3, is the most important factor in the ionization process of 3,4-$(OH)_2PhCOOH$. Indeed, it is well known that the introduction of the hydroxyl group in position 3 destabilizes the benzene ring, so overcoming the stabilization effect caused by the hydroxyl group in position 4. Finally, a statistical comparison between the 3,4-dihydroxy derivative and the 3-monohydroxy and 4-monohydroxy derivatives can give a deeper insight into the understanding of the behaviour of monosubstituted and disubstituted hydroxy derivatives.

Ionization processes

A diparametric regression equation between the respective ionization enthalpy values shows how (Table 12) the standard deviation of the coefficient of the 4-hydroxy derivative (Too large with respect to its slope value) indicates that b_1 and b_2 cannot be compared. There is also a good correlation between ΔH_3 and ΔH_4 (high collinearity) (Table 13). The monoparametric regression between $\Delta H_{3,4}$ and ΔH_3 is highly significant while that between $\Delta H_{3,4}$ and ΔH_4 is significant (Table 13).

Solvation processes of undissociated molecules

Considering the comparison of solvation of undissociated molecules by means of the diparametric relation, the standard deviations of the b_1 and b_2 coefficients (both small with respect to the slope values) show that these are comparable (Table 14). However, the high significance of the monoparametric relation between ΔH_3 and ΔH_4 excludes this comparability (Table 15).

TABLE 12

Results of the diparametric regression analysis of the ionization process for 3,4-dihydroxybenzoic acid as a function of the 3- and 4-hydroxy derivative ionization processes

n	8
a	−0.15
b_1	0.37
b_2	0.18
SD(a)	0.86
SD(b_1)	0.17
SD(b_2)	0.24
SD of regression	1.25
r	0.93
F	16.00 [a]

[a] $F > F_{CL,2,n-3}$ at CL > 0.99.

TABLE 13

Results of the monoparametric regression analysis of the ionization process for 3,4-dihydroxybenzoic acid as a function of the 3- and 4-hydroxy derivative ionization processes

	ΔH_3 vs. ΔH_4	$\Delta H_{3,4}$ vs. ΔH_3	$\Delta H_{3,4}$ vs. ΔH_4
n	8	8	8
Intercept	−0.74	0.23	−0.41
Slope	1.23	0.48	0.64
SD of intercept	1.89	0.72	1.05
SD of slope	0.24	0.08	0.13
SD of regression	2.77	1.22	1.53
r	0.89	0.92	0.87
nh: intercept = 0	CL < 0.95	CL < 0.95	CL < 0.95
nh: slope = 0	0.99 < CL < 0.999	CL > 0.999	0.99 < CL < 0.999
nh: $r = 0$	0.99 < CL < 0.999	CL > 0.999	0.99 < CL < 0.999

TABLE 14

Results of the diparametric regression analysis of the undissociated molecule solvation process for 3,4-dihydroxybenzoic acid as a function of 3- and 4-hydroxy derivative molecule solvation processes

n	8
a	0.41
b_1	4.08
b_2	2.59
SD(a)	0.75
SD(b_1)	1.49
SD(b_2)	1.36
SD of regression	0.57
r	0.99
F	123.13 [a]

[a] $F > F_{CL,2,n-3}$ at CL > 0.999.

TABLE 15

Results of the monoparametric regression analysis of the undissociated molecule solvation process for 3,4-dihydroxybenzoic acid as a function of the 3- and 4-hydroxy derivative molecule solvation processes

	ΔH_3 vs. ΔH_4	$\Delta H_{3,4}$ vs. ΔH_3	$\Delta H_{3,4}$ vs. ΔH_4
n	8	8	8
Intercept	−0.45	−0.80	−1.39
Slope	0.92	1.28	1.17
SD of intercept	0.10	0.47	0.43
SD of slope	0.02	0.09	0.01
SD of regression	0.16	0.68	0.83
r	0.99	0.98	0.98
nh: intercept = 0	$0.99 < CL < 0.999$	$CL < 0.95$	$0.95 < CL < 0.99$
nh: slope = 0	$CL > 0.999$	$CL > 0.999$	$CL > 0.999$
nh: $r = 0$	$CL > 0.999$	$CL > 0.999$	$CL > 0.999$

TABLE 16

Results of the diparametric regression analysis of the ion solvation process for 3,4-dihydroxybenzoic acid as a function of for 3- and 4-hydroxy derivative ion solvation processes

n	8
a	−0.39
b_1	−0.35
b_2	−0.42
SD(a)	1.90
SD(b_1)	0.27
SD(b_2)	0.46
SD of regression	1.69
r	0.54
F	0.87 [b]

[a] $F > F_{CL,2,n-3}$ at CL > 0.95.

TABLE 17

Results of the monoparametric regression analysis of the ion solvation processes for 3,4-dihydroxybenzoic acid as a function of the 3- and 4-hydroxy derivative ion solvation processes

	ΔH_3 vs. ΔH_4	$\Delta H_{3,4}$ vs. ΔH_3	$\Delta H_{3,4}$ vs. ΔH_4
n	8	8	8
Intercept	4.97	−1.75	−2.11
Slope	−0.41	−0.30	−0.27
SD of intercept	2.10	1.14	1.45
SD of slope	0.69	0.25	0.48
SD of regression	2.58	1.66	1.79
r	−0.23	−0.43	−0.23
nh: intercept = 0	$0.95 < CL < 0.99$	$CL < 0.95$	$CL < 0.95$
nh: slope = 0	$CL < 0.95$	$CL < 0.95$	$CL < 0.95$
nh: $r = 0$	$CL < 0.95$	$CL < 0.95$	$CL < 0.95$

Solvation processes of ions

There are no correlations between the ions of the 3,4-$(OH)_2$PhCOOH, 3-(OH)PhCOOH and 4-(OH)PhCOOH derivatives. Indeed, no correlation for diparametric and monoparametric relations between the above-cited compounds was found (Tables 16 and 17).

These results are in agreement with the fact that the key factors for the ionization processes for the monosubstituted and disubstituted hydroxy derivatives are, respectively, the solvation of the ions and the solvation of the undissociated molecules.

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