

**THERMODYNAMIC STUDY OF THE WATER–DMSO SYSTEM.  
PART I. FEATURES OF THE SYSTEM: THERMODYNAMICS, LINEAR  
FREE-ENERGY RELATIONSHIP AND *ORTHO*-EFFECTS OF SOME  
SUBSTITUTED BENZOIC ACIDS IN THE SYSTEM**

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**ABSTRACT**

A thermodynamic study of the water–dimethylsulfoxide (DMSO) system is presented.

The features of the system are investigated by means of calorimetric and potentiometric measurements.

The thermodynamics of the proton transfer process of mono-substituted benzoic acids, the linear-free energy relationship between *meta* and *para* derivatives, and *ortho*-effects are also presented.

**INTRODUCTION**

In the liquid phases the dissociation of acids has been widely investigated. However, an exhaustive theory of the medium effect on the reagent products has not yet been developed.

It is known that both the undissociated molecules and the ions are completely surrounded by a cluster of solvent molecules. These greatly decrease the electric forces, which, in the gaseous phase, are responsible for the collisions between the reagent products. In the liquid phase, before the molecules and the ions of the reagent could come into contact with each other, the cluster of the solvent molecules must be partially reduced. The different behaviour of the same reagent compounds, in different solvents, can be explained taking into account the different solvations.

Dipolar aprotic solvents are unable to form hydrogen bonds, but they have dipolar moments large enough to stabilize anions in solution. These solvation clusters are weaker than those of protic solvents, so that some

reactions in dipolar aprotic solvents tend to resemble those in the gaseous phase.

Proton transfer is the most general and important reaction in chemistry, so that, in turn, it is important to know how acid-base reactions are influenced by the solvent.

DMSO (dimethylsulfoxide)-water solutions with mole fractions,  $X_{\text{DMSO}}$ , ranging from 0.0 to 0.8 constitute a very suitable system for studying the solvation of both the ions and undissociated molecules. Furthermore, water has always been considered as a suitable solvent for most reactions. DMSO, in turn, has many uses as a medium for chemical reactions [1] since it is a powerful solvent for many organic and inorganic compounds.

## FEATURES

During recent years, many kinetic [2-5] and thermodynamic [6,7] investigations have been performed on  $\text{H}_2\text{O}$ -DMSO mixtures. The integral enthalpy of mixing of various amounts of water and DMSO have been previously reported by Drinkard and Kivelson [8], Kenttamaa and Lindberg [9], and Cowie and Toporowsky [10]; the partial molar enthalpy of solution of water at infinite dilution in DMSO has been measured by Arnett and McKelvey [11].

From calorimetric measurements of the partial molar enthalpy of pure DMSO and  $\text{H}_2\text{O}$  in solutions with various mole fractions [12], it can be inferred that water-DMSO interactions do not lead to a stoichiometric compound.

Water behaves towards DMSO as a structure-breaker, and DMSO added in small amounts to water shows the properties of a strong structure-maker.

Enthalpies of reaction between  $\text{H}_2\text{O}$  and DMSO in dilute dioxane solutions have been measured [13] in the presence of excesses of both DMSO and water, at various excess concentrations with a constant concentration of limiting component. The experimental results do not agree with the hypothesis of formation of the compound  $2\text{H}_2\text{O} \cdot \text{DMSO}$ , but are consistent with the existence of weak and non-specific interactions leading to a 1 : 1 equivalent adduct.

The autoprotolysis of water in a mixed solvent (at  $25^\circ\text{C}$ ) was studied by potentiometric [6,14-16] and calorimetric [17] methods at various mole fractions of DMSO-water.

It can be concluded even with respect to the ionization of water, that DMSO-water mixtures can be divided into three zones [18]: (1)  $X_{\text{DMSO}} = 0.0-0.15$ , with an ordered structure favourable for dissociation, but with a lower solvation power than that of pure water; (2)  $X_{\text{DMSO}} = 0.15-0.5$ , with a greater solvating power but a disordered structure; and (3)  $X_{\text{DMSO}} > 0.5$  with a reinforced structure but a rapid lowering of the solvating ability.

THERMODYNAMICS: FREE ENERGY, ENTHALPY AND ENTROPY OF SOME SUBSTITUTED BENZOIC ACIDS

In view of the fact that structural modifications and ionic solvation can be detected from free-energy and calorimetric measurements [19–26] related to the ionization process of weak acids, a thermodynamic study of the following acids, in the DMSO–H<sub>2</sub>O system, was carried out: (1) benzoic; (2) *o*-Cl-benzoic; (3) *m*-Cl-benzoic; (4) *p*-Cl-benzoic; (5) *o*-NO<sub>2</sub>-benzoic; (6) *m*-NO<sub>2</sub>-benzoic; (7) *p*-NO<sub>2</sub>-benzoic; (8) *o*-OH-benzoic; (9) *m*-OH-benzoic; (10) *p*-OH-benzoic; (11) *o*-CH<sub>3</sub>O-benzoic; (12) *p*-CH<sub>3</sub>O-benzoic.

In Tables 1–3, the  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$  values of these acids at various mole fractions are reported. It is evident that the enthalpic term is more

TABLE 1

Free-energy values of ionization for substituted benzoic acids in water–DMSO solutions at 25°C

$X_{\text{DMSO}} =$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
Benzoic acid	5.73	6.37	7.11	7.99	8.93	9.87	10.80	11.74	
<i>o</i> -Cl	4.01	4.95	5.95	6.84	7.65	8.25	9.41	10.15	10.92
<i>m</i> -Cl	5.23	5.72	6.37	7.23	8.22	8.78	9.70	10.53	11.11
<i>p</i> -Cl	2.87	5.78	6.44	7.35	8.44	9.16	10.09	10.80	11.60
<i>o</i> -NO <sub>2</sub>	2.96	3.91	4.79	5.65	6.47	7.24	8.01	8.77	9.37
<i>m</i> -NO <sub>2</sub>	4.74	5.15	5.68	6.36	7.13	7.91	8.70	9.49	10.16
<i>p</i> -NO <sub>2</sub>	4.70	5.10	5.67	6.38	7.20	8.06	8.84	9.61	10.20
<i>o</i> -OH	4.10	4.44	4.70	5.17	5.62	6.16	6.72	7.35	7.90
<i>m</i> -OH	5.56	6.35	7.11	7.97	8.91	9.78	10.86	11.90	12.70
<i>p</i> -OH	6.25	6.95	7.78	8.92	9.67	11.52	11.52	11.77	13.67
<i>o</i> -CH <sub>3</sub> O	5.53	6.48	7.41	8.38	7.38	10.25	11.53	12.18	12.85
<i>p</i> -CH <sub>3</sub> O	6.09	6.26	7.57	8.62	7.23	9.88	10.97	12.17	13.10

TABLE 2

Enthalpy values of ionization for substituted benzoic acids in water–DMSO solutions at 25°C

$X_{\text{DMSO}} =$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
Benzoic acid	0.1	0.48	1.21	1.88	2.43	3.38	3.30	4.29	6.07
<i>o</i> -Cl	-2.50	-1.26	2.95	2.81	3.12	4.17	7.73	12.72	11.95
<i>m</i> -Cl	0.03	0.26	2.15	3.75	2.46	5.56	6.93	7.13	11.89
<i>p</i> -Cl	0.25	0.41	2.03	4.99	5.27	3.18	4.20	7.24	11.66
<i>o</i> -NO <sub>2</sub>	-0.78	0.24	0.87	4.04	5.48	10.49	7.57	7.52	9.49
<i>m</i> -NO <sub>2</sub>	5.30	2.10	6.67	10.43	14.61	16.12	16.53	11.94	12.50
<i>p</i> -NO <sub>2</sub>	4.52	0.65	1.50	6.76	7.15	6.58	7.94	10.18	15.90
<i>o</i> -OH	0.73	0.79	1.94	3.36	8.15	8.27	8.46	11.59	9.96
<i>m</i> -OH	0.16	1.46	4.36	3.74	7.12	9.97	12.43	15.69	13.80
<i>p</i> -OH	0.37	1.16	4.64	6.14	8.58	9.57	9.57	10.04	11.89
<i>o</i> -CH <sub>3</sub> O	0.05	0.84	2.53	4.81	7.38	9.95	12.20	13.85	15.59
<i>p</i> -CH <sub>3</sub> O	0.6	0.91	2.58	4.89	7.23	10.08	12.76	14.13	13.60

TABLE 3

Entropy values of ionization for substituted benzoic acids in water–DMSO solutions at 25°C

$X_{\text{DMSO}} =$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
Benzoic acid	-5.63	-5.89	-5.23	-6.11	-6.50	-6.49	-7.50	-7.45	-6.42
<i>o</i> -Cl	-6.50	-3.00	-4.03	-4.53	-4.08	-1.68	-1.68	2.57	1.03
<i>m</i> -Cl	-5.16	-5.46	-4.22	-3.48	-5.76	-3.22	-2.74	-3.40	+0.78
<i>p</i> -Cl	-2.62	-5.37	-4.41	-2.36	-3.17	-5.98	-5.89	-3.56	0.06
<i>o</i> -NO <sub>2</sub>	-3.74	-3.67	-3.92	-1.61	-0.99	+3.25	-0.44	-1.25	+0.09
<i>m</i> -NO <sub>2</sub>	0.56	-3.05	0.99	4.07	7.48	8.21	7.83	2.45	2.34
<i>p</i> -NO <sub>2</sub>	-0.18	-4.45	-4.17	+0.38	-0.05	-1.48	-0.90	0.57	5.74
<i>o</i> -OH	-3.37	-3.65	-2.76	-1.81	2.53	2.08	1.74	4.22	2.06
<i>m</i> -OH	-5.40	-4.89	-2.75	-4.23	-1.79	0.19	1.48	3.73	1.10
<i>p</i> -OH	-5.88	-5.79	-3.14	-2.78	-1.09	-1.95	-1.95	-1.77	-1.78
<i>o</i> -CH <sub>3</sub> O	-5.48	-5.64	-4.88	-3.57	-1.91	-0.30	0.67	1.67	1.74
<i>p</i> -CH <sub>3</sub> O	-5.49	-5.35	-4.30	-3.74	-2.33	0.20	1.70	1.96	0.50

favourable than the free-energy from pure water up to  $X_{\text{DMSO}} = 0.5$ . Beyond this mole fraction, both terms play equal roles. Furthermore, the *ortho*-derivatives display more favourable free energy and enthalpic terms up to  $X_{\text{DMSO}} = 0.5$ , with the exception of the *o*-OH derivatives for which this is true over the whole mole fraction range. This behaviour can be explained by means of a strong intermolecular hydrogen bond which greatly stabilizes the anion. The same occurs for the *ortho*-nitro derivative. For the *para*-methoxy and the -hydroxy derivatives, the electron-releasing resonance effect weakens the acid strength from the free energy point of view.

Again, for the free-energy term, the inductive effect in the *ortho*-derivatives display the following acid strength sequence: OH > NO<sub>2</sub> > Cl > CH<sub>3</sub>O, while for the enthalpic term the sequence is: Cl > NO<sub>2</sub> > OH > CH<sub>3</sub>O.

It is noteworthy that, at high mole fractions of DMSO, there is an increasing differentiation in the acidity of substituted and unsubstituted benzoic acids, due to a decrease in anion solvation. Thus, the behaviour of the dissociation reactions is similar to that observed in the gas phase. The difference in acidity due to different substituent groups is greatly diminished by the anions' solvation in water-rich solutions. The DMSO–water system is very suitable for emphasizing the influence of the medium on the strength of the acid compounds.

#### LINEAR FREE ENERGY RELATIONSHIP (LFER)

The Hammett equation [27] is the most widely known among the linear free energy relationships. It correlates reaction rates and equilibrium constants for side-chain reactions of *meta*- and *para*-substituted benzene derivatives. Because of the availability of data, the standard reaction chosen was

the dissociation of benzoic acids in water at 25°C. According to Hammett [27] and others [28,29], the following equations may be written



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

where  $X$  is the mole fraction of the solvent. The substituent constant,  $\sigma$ , is considered to be a measure of the ability of the particular group  $X$  to supply or withdraw electrons.

The reaction constant,  $\rho$ , measures the sensitivity of reaction to electron supply or withdrawal.

By separating substituent effects into enthalpic and entropic contributions [30], eqn. (2) may be written in the form

$$-\frac{\delta\Delta G^0}{2.303RT} = \rho_H\sigma_H + \rho_S\sigma_S \quad (3)$$

where

$$\rho_H\sigma_H = -\frac{\delta\Delta H^0}{2.303RT} \quad (3a)$$

$$\rho_S\sigma_S = \frac{\delta\Delta S^0}{2.303R} \quad (3b)$$

Thus it is possible to study the behaviour of *meta* and *para* isomers by means of the effect of the medium on the reaction and substituent constants. The values of  $\sigma_m$ ,  $\sigma_p$ ,  $\sigma_o$ ,  $\sigma_H$ ,  $\sigma_S$  and  $\rho_S$  of meta, para and ortho derivatives are reported in Tables 4–7.

For all *meta* and *para* derivatives the reaction constants,  $\rho_{m,p}$  (calculated by using free energy values), fall on a straight line [31,32]. This is due to decreased anion solvation which, as previously show, is related to an increasing differentiation in the acidity of substituted benzoic acids. In this

TABLE 4

$\sigma$  values for substituted benzoic acids in water–DMSO mixtures at 25°C

$X_{\text{DMSO}}$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
<i>o</i> -Cl	0.292	0.426	0.388	0.344	0.384	0.501	0.421	0.406	0.365
<i>m</i> -Cl	0.370	0.391	0.397	0.358	0.318	0.457	0.427	0.428	0.441
<i>p</i> -Cl	0.210	0.354	0.362	0.302	0.220	0.297	0.275	0.335	0.284
<i>o</i> -NO <sub>2</sub>	0.630	0.785	0.869	0.780	0.799	0.814	0.807	0.807	0.781
<i>m</i> -NO <sub>2</sub>	0.736	0.737	0.774	0.757	0.805	0.821	0.815	0.791	0.746
<i>p</i> -NO <sub>2</sub>	0.755	0.768	0.779	0.761	0.774	0.758	0.761	0.749	0.733
<i>o</i> -OH	-0.434	-0.186	-0.031	0.08	0.265	0.148	0.430	0.543	0.581
<i>m</i> -OH	0.125	0.012	0.000	0.010	0.009	0.038	-0.023	-0.057	-0.067
<i>p</i> -OH	-0.381	-0.350	-0.363	-0.438	-0.331	-0.691	-0.376	-0.373	-0.299
<i>o</i> -CH <sub>3</sub> O	-0.248	-0.036	-0.309	-0.356	-0.336	-0.174	-0.304	-0.266	-0.248
<i>p</i> -CH <sub>3</sub> O	-0.260	0.064	-0.250	0.299	-0.284	-0.003	-0.064	-0.153	-0.154

TABLE 5

 $\sigma_H$  values for substituted benzoic acids in water–DMSO mixtures at 25°C

$X_{\text{DMSO}} =$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
<i>o</i> -Cl	-0.0068	-0.11	-0.098	-0.084	-0.097	-0.132	-0.108	-0.104	-0.091
<i>m</i> -Cl	-0.092	-0.099	-0.101	-0.089	-0.077	-0.119	-0.110	-0.110	-0.114
<i>p</i> -Cl	-0.044	-0.088	-0.090	-0.072	-0.047	-0.070	-0.064	-0.082	-0.066
<i>o</i> -NO <sub>2</sub>	-0.178	-0.219	-0.245	-0.218	-0.223	-0.228	-0.226	-0.266	-0.216
<i>m</i> -NO <sub>2</sub>	-0.203	-0.207	-0.216	-0.213	-0.225	-0.230	-0.229	-0.224	-0.207
<i>p</i> -NO <sub>2</sub>	-0.211	-0.214	-0.217	-0.212	-0.216	-0.21	-0.212	-0.208	-0.204
<i>o</i> -OH	-	-	-	-	-	-	-	-	-
<i>m</i> -OH	-0.044	0.017	0.020	0.017	0.017	0.009	-	-	-
<i>p</i> -OH	-	-	-	-	-	-	-	-	-
<i>o</i> -CH <sub>3</sub> O	-	-	-	-	-	-	-	-	-
<i>p</i> -CH <sub>3</sub> O	-	-	-	-	-	-	-	-	-

TABLE 6

 $\sigma_S$  values for substituted benzoic acids in water–DMSO mixtures at 25°C

$X_{\text{DMSO}} =$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
<i>o</i> -Cl	0.398	0.545	0.504	0.454	0.499	0.627	0.539	0.523	0.935
<i>m</i> -Cl	0.483	0.506	0.513	0.471	0.426	0.579	0.546	0.584	0.561
<i>p</i> -Cl	0.304	0.406	0.474	0.409	0.318	0.403	0.379	0.445	0.389
<i>o</i> -NO <sub>2</sub>	0.791	0.939	1.032	0.934	0.954	0.971	0.963	0.964	0.935
<i>m</i> -NO <sub>2</sub>	0.880	0.887	0.927	0.908	0.962	0.978	0.973	0.955	0.897
<i>p</i> -NO <sub>2</sub>	0.910	0.921	0.933	0.913	0.927	0.910	0.913	0.900	0.883
<i>m</i> -OH	0.168	0.090	0.077	0.088	0.087	0.119	-	-	-
<i>o</i> -OH	-1.807	-0.127	0.043	0.165	0.368	0.240	0.549	0.674	0.715
<i>p</i> -OH	-0.183	-0.309	-0.322	-0.404	-0.287	-0.682	-0.336	-0.33	-0.252
<i>o</i> -CH <sub>3</sub> O	-0.196	0.037	-0.262	-0.314	-0.292	-0.114	-0.257	-0.215	-0.196
<i>p</i> -CH <sub>3</sub> O	0.087	0.147	-0.198	-0.252	-0.235	+0.074	0.004	-0.091	-0.092

TABLE 7

 $\rho_S$  values for substituted benzoic acids in water–DMSO mixtures at 25°C

$X_{\text{DMSO}} =$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
<i>o</i> -Cl	0.292	0.426	0.388	0.344	0.384	0.501	0.421	0.406	0.365
<i>m</i> -Cl	0.912	0.612	2.419	3.936	1.290	4.126	6.282	5.440	9.368
<i>p</i> -Cl	1.038	0.782	2.313	6.526	7.695	0.893	3.085	6.408	11.240
<i>o</i> -NO <sub>2</sub>	0.650	0.785	0.869	0.780	0.799	0.814	0.807	0.807	0.781
<i>m</i> -NO <sub>2</sub>	1.105	2.340	5.445	8.102	10.645	10.992	11.520	7.589	7.146
<i>p</i> -NO <sub>2</sub>	1.100	1.142	1.361	5.124	5.100	4.024	5.279	6.500	9.880
<i>o</i> -OH	1.00	17.480	-54.651	-13.521	1.726	-2.654	-0.717	-1.466	-2.108
<i>m</i> -OH	1.00	8.120	30.050	15.670	29.720	41.11	-	-	-
<i>p</i> -OH	1.00	-2.321	-6.286	-6.035	-13.819	-4.882	-12.586	-7.075	-13.492
<i>o</i> -CH <sub>3</sub> O	-0.248	-0.036	-0.309	-0.356	-0.336	-0.174	-0.304	-0.266	-0.248
<i>p</i> -CH <sub>3</sub> O	1.00	2.694	-3.343	-6.893	-13.00	-	-	-75.76	-52.30

way, the proton transfer process becomes similar to that in the gaseous phase.

As inductive effects for chloro derivatives are much greater than resonance effects, one can expect to find  $\sigma_{m,p}$  values that are independent of, or only slightly affected by, the solvent [31].

The order of substituent constants is  $\sigma_m > \sigma_p$  throughout the mole 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  $\sigma$  values are positive and the *meta* anion is a weaker base than the *para* anion in reaction (1) because of the weaker electron-attractive effect of the chlorine atom in the *para* position. Furthermore, the greater  $\sigma_s$  values (Table 6) with respect to the  $\sigma_H$  values (Table 5) indicate that external contributions are entropy-controlled and therefore chiefly inductive in character [30].

Contrary to the trend of the reaction constants,  $\rho_{m,p}$ , derived from  $\delta\Delta G$  values, the  $\rho_s$  constants show a minimum at  $X_{\text{DMSO}} = 0.4$  and  $0.5$ . This behaviour can be related to a typical feature of DMSO–water solutions [18]. Indeed, at  $X_{\text{DMSO}} = 0.5$  the maximum structure-breaking characteristics displayed by the solution increase the solvating power of the mixture towards the anions, so that the maximum solute–solvent interactions are found at this mole fraction.

The inductive or resonance effects prevail as a function of solvent composition variation for nitro derivatives [32]. In the range  $0.0 \leq X_{\text{DMSO}} \leq 0.3$  the resonance effect is more significant. Beyond  $0.3$  mole fraction, the inductive effect prevails over the resonance effect and the order of substituent constants becomes  $\sigma_m > \sigma_p$ . Unlike the trend of the  $\rho_s$  values of the ionization of chloro benzoic acids, the entropy reaction constants,  $\rho_s$ , do not show a minimum at  $X_{\text{DMSO}} = 0.5$ . The  $\sigma_p$  values of *p*-OH derivatives are greatly affected by solvent composition and by major resonance effects. It should be noted that  $\sigma_m$  values decrease from  $0.0$  to  $0.1$  mole fraction, remain constant in the range  $0.1 \leq X_{\text{DMSO}} \leq 0.57$ , and change their sign beyond this mole fraction. The  $\sigma_p$  values (always negative) show a maximum at  $X_{\text{DMSO}} = 0.5$ . These trends can be rationalized when considering [31] that only if the field effects are much larger than the resonance effect, can  $\sigma$  values be expected to be independent of, or only slightly affected by, the solvent composition.

The entropy reaction constants of the *meta*-hydroxy benzoic acid are much greater than those of the *meta*-chloro and nitro benzoic acids throughout the mole fraction range.

For the  $\sigma_s$  values of the three *meta* derivatives the following order is observed [33] for all mole fractions:  $\sigma_{\text{NO}_2} > \sigma_{\text{Cl}} > \sigma_{\text{OH}}$ . On the basis of the inductive effect, the following order of entropy reaction constants can be expected:  $\rho_{\text{NO}_2} > \rho_{\text{Cl}} > \rho_{\text{OH}}$ , while the observed order is  $\rho_{\text{OH}} > \rho_{\text{Cl}} > \rho_{\text{NO}_2}$ . This behaviour can be ascribed to the larger solvation of the *meta*-hydroxy

anion with respect to the unsubstituted anion. This fact, in turn, is in agreement with the hypothesis that for the hydroxy derivatives, the hydrogen bonding of the hydroxyl group of solvent molecules is more important than the interactions of the nitro and chloro groups with the same molecules. The *para*-hydroxy derivative displays negative  $\sigma_p$  values throughout the mole fraction range. This was related to the electron releasing resonance effect which overlaps and prevails over the inductive effect. It can also be observed that [33] in water at 25°C, for the *meta*-hydroxy compound the entropic contribution,  $f_s$ , is equal to 80% for the total substituent effect, while for the *para*-hydroxy isomer the enthalpic contribution  $f_H = 0.52$  prevails. This clearly shows that the resonance contribution to the substituent effect for the *p*-OH isomer is larger than that for the *m*-OH isomer, indeed the resonance is mainly related to the enthalpic term.

It can be observed that the  $\sigma_p$  values are only greatly affected by the solvent composition in the 0.43–0.58 mole fraction range. Thus, in the same mole fraction range, only approximate values for  $\rho_s$  and  $\sigma_s$  are found.

The electron-releasing resonance effect decreases the equilibrium constant by increasing, and thus localizing, the negative charge of the carboxylate group. The  $\rho_s$  negative values increase as the H<sub>2</sub>O content decreases. This can be related to an enhanced anion desolvation which, in turn, yields an increasing differentiation in the acidity of hydroxy-substituted and unsubstituted benzoic acid.

The *para*-methoxy derivative also shows negative  $\sigma_p$  values throughout the mole fraction range. This was related to the electron-releasing resonance effect which overlaps and prevails over the inductive effect. It can be observed that the  $\sigma$  values are greatly affected by the solvent composition in the 0.2–0.45 mole fraction range. Thus, approximate trends for  $\sigma_s$  and  $\rho_s$  in this mole fraction were found.

The methoxy group shows a weaker resonance as compared to the hydroxyl group. For this reason, the *para*-methoxy anion interacts with the solution molecules less strongly than the hydroxy anion and the negative  $\rho_s$  values of *para*-methoxy benzoic acid increase as the content of H<sub>2</sub>O decreases. This is more marked than the  $\rho_s$  values of the *para*-hydroxy derivative.

#### ORTHO-EFFECTS

The proton transfer process of *ortho* derivatives has been studied by means of a linear combination of the ordinary polar, proximity polar and steric effects [34,35]. Enthalpic and entropic contributions to substituent effects for the *ortho* derivatives have also been examined.

$$-\frac{\delta\Delta G^0}{2.303RT} = \rho_o\sigma_o + fF + \delta E_s \quad (4)$$



The ordinary polar effect would be imaginary from *ortho* substituent effects without the proximity polar and steric effects. The ordinary polar effect is equal, by definition, to that of the *para* substituents, so that  $\sigma_o \equiv \sigma_p$ . The proximity polar effect,  $F$ , would account for the inductive and field effects. The steric effect would include the space-filling factor of the *ortho* substituent (primary steric effect) with a consequent steric hindrance to solvation for the functional group (secondary steric effect). The last effect also includes a steric inhibition of the resonance in the substituent or in the functional group (secondary steric effect).

For the *o*-OH and *o*-CH<sub>3</sub>O derivatives modified equations were used.

$$-\frac{\delta\Delta G^0}{2.303RT} = \rho_o\sigma_o^2 + fF + \sigma_o^1 - \sigma_p + \delta E_s \quad (5)$$

where the  $\sigma_o^1 - \sigma_p$  values for the hydroxy derivative are a measure of the field effect, while for the methoxy derivative they are a measure of the steric inhibition of resonance. In this way, it is possible to find the  $\sigma_o$  values on the same scale as  $\sigma_m$  and  $\sigma_p$  (Table 4).

The order of the substituent constants is  $\text{NO}_2\text{-}\sigma_o > \text{Cl-}\sigma_o$  throughout the mole fraction range. Indeed the  $\text{NO}_2$  group is a more powerful electron acceptor than the Cl group.

For the chloro benzoic acid the values of  $\rho_s$  are negative in the mole fraction range 0.0–0.15. This can be ascribed to the more drastic desolvation [36] of the *o*-chloro benzoic anion with respect to the unsubstituted anion in water-rich solutions. On the other hand, beyond 0.15 mole fraction, both anions are desolvated and the  $\rho_s$  values become positive. This behaviour is in agreement with the hypothesis that, for the chloro derivatives, the solvation of the anions, rather than that of the undissociated molecules, is involved in the control of the course of the reaction. However, for the nitrocompounds it seems reasonable to assume that both the undissociated molecules and their anions exhibit a steric inhibition of solvation on the carboxyl and carboxylate groups, respectively.

The primary steric effect on the solvated carboxyl group and the resulting congestion accelerate the dissociation of the neutral molecule. The steric inhibition of solvation for the anions counteracts the steric acceleration effect on the undissociated molecules and tends to reduce the dissociation rate of the compound. This fact explains the very low values of  $o\text{-}\rho_s$  with respect to those of the chloro derivatives beyond 0.5 mole fraction.

Equation (4), used for calculating  $\sigma_o$  values for *o*-Cl and *o*-NO<sub>2</sub> derivatives, is not likely to be effective for the *o*-OH derivatives. Furthermore, for the Cl and NO<sub>2</sub> compounds, the  $\sigma_o$  values are very close to the respective  $\sigma_p$  values, while for the OH derivative this is not the case. This difference can be assumed as a measure of the internal hydrogen bond, so that  $\sigma_o^1 - \sigma_p$  values are included in eqn. (5) as an additional term for the field effect and a better approximation for the substituent constant value,  $\sigma_o^2$ , is found.

It is also known that the hydrogen bonding of the solvent to the  $\text{OCH}_3$  group would hinder the formation of the chelate structure in water and would modify the inductive and field effects of  $\text{OCH}_3$  on the  $\text{COOH}$  group. Therefore, the hydration could increase the bulk of  $\text{OCH}_3$  to such a degree as to cause steric inhibition of the resonance of  $\text{COOH}$ , and of  $\text{OCH}_3$  itself with the benzene ring.

If it is assumed that the secondary steric effect only occurs in the substituent group, then the  $\sigma_o^1 - \sigma_p$  difference can be considered as a measure of the steric inhibition of resonance and can be included in eqn. (5) as an additional term.

For the hydroxy benzoic acid the values of  $\rho_s$  are negative with the exception of the 0.0–0.133 mole fraction range. The reason for this seems to be due to the larger desolvation of the *ortho* anion with respect to the unsubstituted anion. This behaviour shows that for the hydroxy benzoic acid the solvation of the anions is the main factor controlling the course of the reaction.

The *ortho*-methoxy derivative shows negative  $\sigma_s$  values throughout the mole fraction range. This was related to the electron-releasing resonance effect which overlaps and prevails over the inductive effect. Thus, it seems reasonable to conclude that the  $\text{CH}_3\text{O}$  group undergoes a partial steric inhibition of resonance.

If one assumes that the inductive and field effects are the same for the methoxy and hydroxy derivatives,  $\sigma_{o(\text{OH})}^2 - \sigma_{o(\text{CH}_3\text{O})}^2$  should be a measure of the difference between the resonance effects of the two *ortho* derivatives [35]. The  $\text{CH}_3\text{O}$  group displays a greater electron-releasing resonance effect over the whole mole fraction range.

It can be concluded that this study affords the possibility of obtaining a complete picture of the proton transfer process. It is also possible to indicate the factors (inductive, resonance, field, *ortho* effects) which mostly influence the process and how they affect each other.

## REFERENCES

- 1 D. Martin and H.G. Hauthal, Dimethyl Sulphoxide, Van Nostrand Reinhold, Working-am. U.K.
- 2 R.K. Wolford, J. Phys. Chem., 68 (1964) 3392.
- 3 E. Tomila, Acta Chem. Scand., 20 (1966) 923.
- 4 E. Tomila and S. Sovalaynen, Acta Chem. Scand., 20 (1966) 946.
- 5 P. Fiordiponti and F. Rallo, J. Chim. Phys. (1972) 805.
- 6 J. Hallé, R. Gaboriaud and R. Schaal, Bull. Soc. Chim. Fr., (1969) 1851.
- 7 J.P. Morel, J. Chim. Phys., (1970) 895.
- 8 W. Drinkard and D. Kivelson, J. Phys. Chem., 62 (1968) 1494.
- 9 J. Kenttamaa and J.J. Lindberg, Suom. Kem. B, 33 (1960) 32.
- 10 M.G. Cowie and P.M. Toporowshi, Can. J. Chem., 39 (1961) 2240.
- 11 E.M. Arnett and D.K. McKelvey, J. Am. Chem. Soc., 88 (1966) 2598.

- 12 F. Rallo, F. Rodante and P. Silvestroni, *Thermochim. Acta*, 1 (1970) 311.
- 13 F. Rallo and F. Rodante, *Ann. Chim.*, 32 (1972) 221.
- 14 E.M. Woolley, D.G. Hurkot and L.G. Hepler, *J. Phys. Chem.*, 74 (1970) 3908.
- 15 P. Fiordiponti, F. Rallo and F. Rodante, *Z. Phys. Chem., Neue Folge*, 88 (1974) 149.
- 16 C.K. Izutsu, T. Adachi and T. Fujinaga, *Electrochim. Acta*, 15 (1970) 135.
- 17 F. Rodante, F. Rallo and P. Fiordiponti, *Thermochim. Acta*, 6 (1972) 369.
- 18 R.K. Wolfard, *J. Phys. Chem.*, 68 (1964) 3392.
- 19 P. Fiordiponti, F. Rallo and F. Rodante, *Gazz. Chim. Ital.*, 104 (1974) 649.
- 20 F. Rodante, F. Rallo and P. Fiordiponti, *Thermochim. Acta*, 9 (1974) 269.
- 21 F. Rodante and P. Fiordiponti, *Thermochim. Acta*, 19 (1977) 13.
- 22 P. Fiordiponti and F. Rodante, *Ann. Chim.*, 67 (1977) 361.
- 23 F. Rodante, *Thermochim. Acta*, 32 (1979) 293.
- 24 F. Rodante, G. Ceccaroni and M.G. Bonicelli, *Thermochim. Acta*, 42 (1980) 223.
- 25 F. Rodante, G. Ceccaroni and F. Fantauzzi, *Thermochim. Acta*, 59 (1982) 253.
- 26 F. Rodante, *Thermochim. Acta*, 67 (1983) 45.
- 27 L.P. Hammett, *Physical Organic Chemistry*, McGraw-Hill/Kogakusha, New York, 1970.
- 28 H.H. Jaffé, *Chem. Rev.*, 53 (1953) 191.
- 29 T. Matsui, H. Chung Ko and L.G. Hepler, *Can. J. Chem.*, 53 (1974) 2906.
- 30 T.M. Krygowski and W.R. Fawcett, *Can. J. Chem.*, 53 (1975) 3622.
- 31 F. Rodante, *Thermochim. Acta*, 31 (1979) 221.
- 32 F. Rodante, *Thermochim. Acta*, 34 (1979) 29.
- 33 F. Rodante, G. Ceccaroni and M.G. Bonicelli, *Thermochim. Acta*, 43 (1981) 199.
- 34 F. Rodante and G. Pistoia, *Thermochim. Acta*, 43 (1981) 325.
- 35 F. Rodante, G. Ceccaroni and F. Fantauzzi, *Thermochim. Acta*, 67 (1983) 45.
- 36 F. Rodante, *Thermochim. Acta*, 34 (1979) 377.