Study of the Hammett Equation for the Ionisation of Substituted Benzoic Acids and Phenols in Dioxan–Water Mixtures

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The thermodynamic p*K* values of 17 substituted benzoic acids and 21 substituted phenols were determined in 20, 40, 60, and 80% v/v dioxan–water at 30 ± 0.1 °C and μ 0.1 M ($NaClO_4$) by the Calvin–Bjerrum potentiometric titration technique. The 'practical' p*K* values of substituted benzoic acids were also determined in 85 and 90% v/v dioxan–water mixtures. The Hammett substituent constants were calculated and the data for the *meta*- and *para*-derivatives were utilized to give Hammett reaction constants. It was observed that $d\rho/dD$ (D = dielectric constant) was not regular. In the case of the benzoic acids, the ρ values decrease above 0.44 mole fraction dioxan. The ρ values are, however, insensitive to the medium for *ortho*-substituted compounds. Attempts have been made to explain these observations by considering the structure of the dioxan–water solvent.

THE effects of substitution on the dissociation constants of organic acids have been extensively studied by many workers since the proposal of the Hammett equation.[1] The Hammett ρ value is known to be dependent on the nature of the solvent.[2,3] Explanations of the effect of solvent on ρ values and on rates and equilibria of reactions have been attempted. The importance of solvent reorientation in the activation process has also received attention in recent years.[4,5] This paper presents a systematic study of ionisation of substituted benzoic acids and phenols in dioxan–water. The choice of dioxan as a cosolvent was made for two reasons: (i) the relatively higher solubility of various compounds in dioxan and (ii) the possibility of obtaining dioxan–water mixtures covering a wide range of dielectric constants between 7 and 78. The experimental data can be used in the study of co-ordination complexes of aromatic carboxy- and hydroxy-compounds in solution.

EXPERIMENTAL

All chemicals were either of analytical reagent grade or properly purified. Substituted benzoic acids and phenols were obtained from B.D.H. and Schuchardt. 1,4-Dioxan was purified by the standard procedure.[6] The details of instrumentation and the procedure adopted for potentiometric titrations were given in an earlier paper.[7]

The B values (pH-meter readings in dioxan–water) were converted into $[H^+]$ values by applying the corrections proposed by Van Uitert and his co-workers.[8,9]

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RESULTS

The proton–ligand formation number, $\bar{n}_A$, was calculated by the method of Irving and Rossotti.[10] The expression $\log [\bar{n}_A/(1 - \bar{n}_A)] = pK_1 - pH$ was solved for $\bar{n}_A$ values between 0.8 and 0.2. On an average 5—6 points were taken for each graph. All the points invariably fell on a straight line, whose correlation coefficient was very close to 1. Two sets of potentiometric titration experiments were performed for each system. The precision of the experimental data was checked by comparing the $\bar{n}_A$ values at different pH in the two sets. The standard deviation of these for two representative systems, *i.e.* benzoic acid in 20% v/v dioxan–water and *o*-nitrophenol in 40% v/v dioxan–water were 0.029 and 0.019 in pH ranges 4—5 and 7—8, respectively. The pK values are presented in Table 1.

TABLE 1

(*a*) pK Values (±0.01—0.04) of substituted benzoic acids. Temp. 30 ± 0.1 °C; μ 0.1M ($NaClO_4$)

	% Dioxan (v/v)			
Substituent	20	40	60	80
None	4.83	5.67	7.12	9.22
o-Cl	3.72	4.64	6.12	8.22
m-Cl	4.60	5.30	6.63	8.74
p-Cl	4.49	5.18	6.66	8.89
o-Br	3.94	4.55	5.93	7.91
m-Br	4.66	5.11	6.78	8.42
p-Br	4.53	5.24	6.83	9.03
o-I	4.21	4.70	6.14	8.14
m-I	4.19	5.11	6.61	8.28
p-I	4.39	5.37	6.95	8.98
o-NO_2	3.11	3.97	5.28	7.63
m-NO_2	4.12	4.64	6.02	8.12
p-NO_2	4.04	4.66	5.99	8.15
o-NH_2	5.16	6.10	7.49	9.63
m-NH_2	4.93	5.82	7.15	9.19
p-NH_2	5.51	6.44	7.90	10.21
3,5-$(NO_2)_2$	3.44	3.68	5.33	7.12

(*b*) pK Values (±0.01—0.06) of substituted phenols. Temp. 30 ± 0.1 °C; μ 0.1M ($NaClO_4$)

None	10.96	11.50	12.36	14.70
o-Cl	8.97	9.86	10.99	12.78
m-Cl	9.67	10.43	11.67	13.56
p-Cl	9.75	10.61	11.51	13.64
o-NO_2	7.33	8.12	9.23	11.38
m-NO_2	8.82	9.14	10.60	12.35
p-NO_2	7.33	8.09	9.03	10.86
o-NH_2	10.45	10.96	12.46	14.67
m-NH_2	10.54	11.43	12.64	14.70
p-NH_2	11.12	11.85	13.67	15.27
o-OH	10.05	10.63	11.90	13.72
m-OH	10.06	10.86	12.31	14.34
p-OH	10.81	11.47	12.78	14.86
2,3-Cl_2	8.34	9.06	10.26	12.41
2,4-Cl_2	8.62	9.35	10.97	12.77
2,5-Cl_2	7.88	8.96	10.59	12.50
2,6-Cl_2	7.51	8.25	9.45	11.52
3,4-Cl_2	9.13	9.95	11.11	13.27
3,5-Cl_2	8.94	9.51	10.25	12.70
2,4-$(NO_2)_2$	4.52	4.93	5.95	7.71
4-Cl-2-NO_2	6.89	7.48	8.58	10.45

DISCUSSION

The accuracy of the experimental data was checked by comparing the pK values obtained by extrapolating the straight line plot of pK against mole fraction dioxan to zero mole fraction with the known literature values.[11] The agreement between the two is satisfactory.

The ΔpK ($pK_{parent} - pK_{subs}$) values for substituted benzoic acids and phenols at different dioxan-water percentages were obtained from the pK values in Table 1 (ΔpK in water for benzoic acid is equal to σ). For substituted benzoic acids, the ΔpK values were also determined in 85 and 90% dioxan-water mixtures [$\mu \sim 0.05$M ($NaClO_4$)]. These ΔpK values represent the differences between the ' practical ' and not the ' thermodynamic ' values as correction factors are not available for such high percentages of dioxan. Despite this limitation, these values are expected to give a correct estimate of ΔpK as the magnitude of the correction factor would probably be the same for the parent and its substituted derivative at high percentages of dioxan. The pK values for phenols were not determined at these percentages because of the insensitivity of the glass electrode above pH 12.0.

Calculations of Hammett Reaction Constants.—The plots of ΔpK against σ were drawn to give ρ values at different dioxan-water percentages. Two straight line plots, one for *meta*- and *para*-derivatives and the other for *ortho*-derivatives, were obtained. The Hammett equation being strictly valid for *meta*- and *para*-substituted compounds, ρ values were calculated by the method of least squares from the linear plot for these compounds. The correlation coefficients were found to be between 0.92 and 0.98. The ρ values are set out in Table 2. The observed value for phenol in aqueous medium is in good agreement with the literature value.[12] The ρ values show a rising trend up to 80% dioxan and then register a fall.

TABLE 2

Hammett reaction constants (ρ) for substituted benzoic acids and phenols in dioxan–water mixtures. Temp. 30 ± 0.1 °C; μ 0.1M ($NaClO_4$)

	ρ	
% Dioxan	Benzoic acids	Phenols
0	1.00[a]	2.23[b]
20	1.07	2.41
40	1.30	2.74
60	1.42	2.83
80	1.68	3.12
85	1.37	
90	1.29	

[a] Lit.[12] 1.00. [b] Lit.[12] 2.26.

Wynne-Jones[13] obtained an inverse relationship between ρ values and the dielectric constant of the solvent. Kilpatrick and his co-worker[14] suggested that this relationship was limited to solvents with $D > 25$. In our studies, a plot of ρ against $1/D$ was nonlinear over the entire range dioxan–water compositions (Figure 1). The plot of ρ against mole fraction (N) dioxan, however, exhibited a different pattern (Figure 2). For benzoic acid, a linear plot was obtained up to 60%

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dioxan, while points corresponding to 80, 85, and 90% dioxan were falling roughly on another straight line. All the points from 0 to 90% dioxan taken together may, however, be considered to be lying on a parabola. The relation between ρ and mole fraction dioxan is given in Table 3.

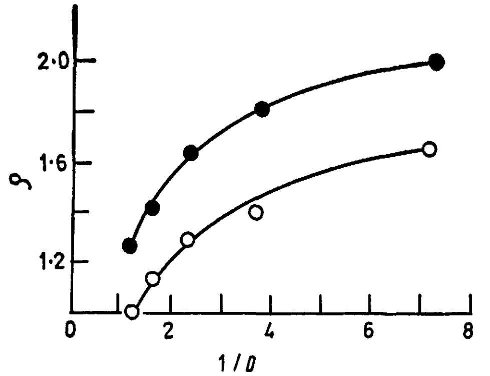

FIGURE 1 Plots of ρ against $1/D$ for substituted benzoic acids (○) and phenols (●). Add 1.0 to the y-axis scale for ρ values of phenols

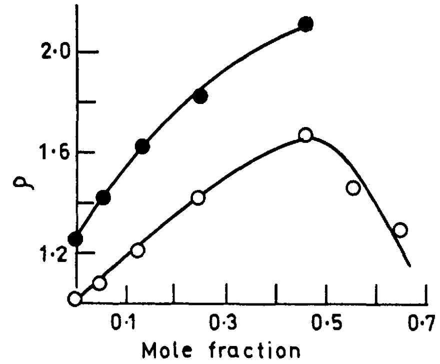

FIGURE 2 Plots of ρ against mole fraction dioxan for substituted benzoic acids (○) and phenols (●)

TABLE 3

Mathematical equations for Hammett reaction constants. Temp. 30 ± 0.1 °C; μ 0.1M ($NaClO_4$)

	% Dioxan	ρ–N	ρ–$1/D$
Benzoic acid	(a) 0—80	$\rho = 1.0 + 1.75N$	$\rho = 0.72 + 23/D$
	(b) 80—90	$\rho = 3.0 + 2.8N$	$\rho = 1.30 + 6/D$
Phenol	0—80	$\rho = 2.26 + 2.8N$	$\rho = 1.86 + 33/D$

A decrease in dielectric constant of the solvent should normally lead to an increase in ρ values. The contrary observation above 80% of dioxan (0.44 mole fraction) in the case of benzoic acid is, therefore, interesting. Tokura and his co-workers[2] have attributed the variation of ρ values with the properties of the solvent to the cross interaction of σ with ξ (where ξ is defined as log $K_0^{\text{other solvent}}/K_0^{\text{water}}$). They arrived at this conclusion on the basis of their observation that: $(\partial\rho/\partial\xi)_0 = (\partial\xi/\partial\sigma)_0$. Our results, however, lead to the conclusion that the variation of ρ with the properties of the solvent does not arise by the cross-interaction between ρ and ξ.

The increase in the ρ with the decrease in the dielectric constant of the medium may either be due to change in the overall dielectric constant of the medium or due to specific solvation effect. If the ' ring solvation ' of the parent acid is unaltered in the substituted compounds, then the plot of $\log K_{\text{subs.}}^{\text{other solvent}}/K_{\text{subs.}}^{\text{water}}$ against $\log K_{\text{parent}}^{\text{other solvent}}/K_{\text{parent}}^{\text{water}}$ should give a straight line with unit slope. Such linear plots were observed for substituted benzoic acids and phenols with slopes ranging from 0.96 to 1.00 for benzoic acids and around 1.08 for phenols. The effect of solvent on the parent and its substituted derivative is, therefore, almost the same for benzoic acids and phenols.

In dioxan–water, there is a greater probability of water molecules occupying the solvation sites in preference to dioxan. However above 80% dioxan, when the molarities of the two solvents become almost equal, the dioxan molecules may probably occupy the charged site in the molecule or its anion. In the plots of $pK_{\text{water}}/pK_{\text{other solvent}}$ against $1/D$, the points corresponding to $D > 25$ fall outside the straight line. The magnitude of the microdielectric constant for the mixture with 80% dioxan as calculated by the procedure of Robinson *et al.*[15] was 28. This suggests the orientation of dioxan molecules in the boat form at high percentages of dioxan.

ortho-*Effect*.—The effect of *ortho*-substitution on the ionisation of benzoic acids in different mixed solvents has been examined by Bowden[16,17] and Charton.[18,19] The analysis of our results on similar lines showed that the ρ values (designated as ρ_o for *ortho*-substitution) remain almost constant at 2.3 up to 60% dioxan, fall to 2.1 at 80%, and then increase to 2.4 at higher dioxan percentages. Our results at lower percentages of dioxan are in agreement with Bowden's observations.[16] The marked sensitivity of ρ to solvent for the *meta*- and *para*-substitution and its near insensitivity to *ortho*-substitution up to 70% dioxan confirm the findings of Bowden[16] that no significant part of transmission of the substituent polar effect occurs through the medium for *ortho*-substitution. The *ortho*-effect was not examined for substituted phenols because of limited number of compounds of this type.

Principle of Additivity.—The principle of additivity[20] was examined for disubstituted phenols and was found to be invalid. It seems that the principle is not valid for 2,3- and 2,6-disubstituted compounds in dioxan–water mixtures as in water.

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