

Dependence of Hammett Constant ρ on Dielectric Constant & Water Activity in Mixed Aqueous Solvents

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pK values of several *m*- and *p*-substituted salicylic acids, anilinium and pyridinium ions have been determined in dioxane-water mixtures potentiometrically. The pK values for benzoic acids and phenols have been determined earlier. The consolidated data have been utilised to obtain values of Hammett constant (ρ). The magnitude of $\Delta\rho (= \rho_s - \rho_w)$ has been found to be almost equal for the five series in 10, 20, 40 and 60% dioxane-water mixtures. The variations of $\Delta\rho$ with the dielectric constant (D) of the solvent mixtures follow an empirical relationship ($\Delta\rho = 19.34 1/D - 0.201$). This relation is designated as Jahagirdar-Arbad-Kharwadkar (JAK) relation. The validity of this equation in different alcohol-water mixtures has been examined and its utility in predicting pK values of substituted compounds has been examined. It is observed that this equation is valid for solvent mixtures having mol fraction of water more than 0.5.

Linear free energy relationships have had a profound impact on the development of physical organic chemistry. The classification of substituent effects on reaction equilibria has led to many accepted concepts on bonding and electronic effects¹. The most widely known attempt to systematize interpretation of acid-base data particularly for free energies and equilibrium constants is the Hammett equation^{2,3}: $\log (K/K^\circ) = \rho\sigma$. The substituent constant σ depends primarily on the nature of the substituent and to a lesser degree on its position, and is assumed to be independent of temperature and solvent. The parameter ρ depends on a particular reaction series under consideration and also on solvent and temperature⁴.

Earlier, the present authors⁵ reported variation in ρ -values for benzoic acid and phenol series in different dioxane-water mixtures. Contrary to the usual belief that ρ should increase with the decrease in dielectric constant of the medium, in our investigations⁵ in water-dioxane media ρ -values decreased after the mol fraction of dioxane reached 0.45, for the benzoic acid series⁵. The earlier study has now been extended to substituted salicylic acids, pyridinium and anilinium ions. Thus the pK values have been determined for the dissociation of neutral species like phenols and benzoic acids as well as for the charged species like pyridinium and anilinium ions.

Materials and Methods

Substituted salicylic acids and anilines were of AR grade (BDH) and pyridines (99.3% pure) were procured from Aldrich Chemicals, USA. Sodium

hydroxide and sodium perchlorate were of AR grade and aqueous solution of sodium hydroxide was standardised with dried sodium carbonate (AR) via aqueous HCl. Potassium hydrogen phthalate and sodium tetraborate were recrystallised and dried by the standard procedure⁶. 1,4-Dioxane (AR) was purified as usual before use.

The pK values of all the compounds in water-dioxane mixtures were measured potentiometrically using an Elico digital pH meter model L1-100 fitted with glass SCE electrode assembly. When not in use, the glass electrode was kept immersed in a solvent mixture of identical composition to the one being studied. The accuracy of the pH measurement was ± 0.01 pH unit. The pH meter was standardised against potassium hydrogen phthalate buffer ($N/20$ with a pH of 4.01 at 30°C) and sodium tetraborate (pH 9.11 at 30°C) and checked by titrating 0.025 *N* HClO₄ against standard NaOH. The pH meter readings were converted to $[H^+]$ from the analytical concentrations of HClO₄ and activity coefficients⁷. The pH meter readings in water-dioxane mixtures (20-80%) were converted into $p\alpha_{H^+}$ by making appropriate corrections proposed by Van Uitert and coworkers^{8,9}.

The Calvin-Bjerrum titration technique¹⁰ was adopted for the determination of pK values of all the compounds. The experimental procedure involved potentiometric titrations of solutions of (i) free HClO₄ (10^{-2} *M*); and (ii) free HClO₄ (10^{-2} *M*) + organic acid (10^{-2} *M*) against standard sodium hydroxide (~ 0.2 *N*) solution. The ionic strength was maintained at ~ 0.1 *M* by the addition of sodium perchlorate solution. All titrations

were carried out at $30 \pm 0.02^\circ\text{C}$ under oxygen-free N_2 blanket. The titrating mixtures were well stirred for 1-2 min and the $p\text{H}$ reading was noted after the stirring was stopped.

The values of \bar{n}_A (proton-ligand formation number) at different $p\text{H}$ values were obtained from the expression¹¹

$$\bar{n}_A = \gamma - \frac{(v_2 - v_1)(N + E^\circ)}{(V^\circ + v_1)T_L^\circ}$$

where V° is the initial volume of the solution; E° and T_L° are the total concentrations of HClO_4 and organic compound, respectively; and v_1 and v_2 are the volumes of alkali of a given normality required during the (i) and (ii) titrations respectively, at a given $p\text{H}$; and γ is the number of replaceable hydrogen atoms in compound and N is the normality of NaOH .

\bar{n}_A values at various $p\text{H}$ were utilized to get pK values, initially by the half-integral method¹¹. The accurate values of pK were determined further by the method of pointwise calculations¹¹. The expression $\log \bar{n}_A / (1 - \bar{n}_A) = pK_1 - p\text{H}$ was used and the values of \bar{n}_A selected were in the range 0.8 to 0.2. Two sets of measurements were taken for every compound and the magnitudes of \bar{n}_A values at specific $p\text{H}$ were compared. The average of the two was taken when the disagreement in the \bar{n}_A value was in the third place of decimal. Whenever the disagreement was in the second place, a third set of experimental measurement was invariably carried out.

Results and Discussion

The pK values of the substituted and the parent compounds in different dioxane-water mixtures presented in Table 1. These correspond to the dissociation of $-\text{COOH}$ group in salicylic acids, $-\text{NH}_3^+$ in anilinium and of $-\text{NH}^+$ in pyridinium ions. The data for benzoic acids and phenols form a part of our earlier publication⁵. The pK values in water were obtained by extrapolation of the linear plot of pK versus mol fraction of dioxane; the pK (W) values thus obtained, exhibit a good agreement with the reported values^{4,12}.

Estimation of ρ -values

The plots of ΔpK ($= pK$ unsubstituted $- pK$ substituted, i.e. $pK_u - pK_s$) against σ were drawn to obtain ρ values. Values of σ were taken from the consolidated table compiled by Shorter¹³. For substituents which involve cross-conjugation σ^n values were used. The plots were linear for each of the series and the correlation coefficient of each

Table 1 — pK Values (± 0.01 to 0.04) of Substituted Organic Compounds

Substituent	Temp. = 303 ± 0.1 K; $\mu = 0.1$ M(NaClO_4)					
	% Dioxane (v/v)					
	0	10	20	40	60	80
(A) Benzoic acid series						
Nil	4.20	4.45	4.73	5.67	7.12	9.22
-m Cl	3.82	4.05	4.40	5.30	6.63	8.75
-p Cl	3.98	4.15	4.49	5.28	6.66	8.89
-m Br	3.85	4.12	4.66	5.51	6.78	8.42
-m I	3.82	3.90	4.19	5.11	6.61	8.28
-p I	3.75	4.15	4.39	5.37	6.95	8.98
-m NO_2	3.40	3.70	3.90	4.64	6.02	8.12
-p NO_2	3.33	3.55	3.74	4.66	5.99	8.15
-m NH_2	4.65	4.80	5.23	5.96	7.15	9.19
-p NH_2	4.93	5.15	5.51	6.44	7.90	10.21
(B) Phenol series						
Nil	10.02	10.70	10.96	11.90	12.36	14.70
-m Cl	9.14	9.40	9.67	10.43	11.67	13.56
-p Cl	9.46	9.58	9.75	10.61	11.51	13.64
-m NO_2	8.38	8.55	8.82	9.14	10.60	12.35
-p NO_2	7.18	7.25	7.33	8.09	9.03	10.86
-m NH_2	9.87	10.25	10.54	11.43	12.64	14.70
-p NH_2	10.30	10.72	11.12	11.85	13.67	15.27
-m OH	9.54	9.90	10.06	10.86	12.31	14.31
(C) Salicylic acid series						
Nil	3.12	3.25	3.37	4.17	5.12	7.42
-4 Cl	2.90	3.10	3.37	3.80	4.76	7.04
-5 Cl	2.69	2.90	3.16	3.71	4.56	6.99
-5 Br	2.70	2.92	3.37	3.86	4.67	6.99
-4 I	2.83	3.00	3.22	3.77	4.96	7.16
-5 I	2.75	2.88	3.19	3.56	4.67	6.45
-5 OH	2.97	3.20	3.51	4.07	5.09	7.35
-5 NO_2	2.30	2.45	2.73	3.00	4.02	6.01
(D) Aniline series						
Nil	4.54	4.50	4.47	4.46	4.45	5.12
-m Cl	3.29	3.35	3.36	3.45	4.08	4.70
-p Cl	3.78	3.93	3.98	4.10	4.51	5.04
-p Br	3.74	3.50	3.59	4.05	4.54	4.82
-m OH	4.37	3.93	4.05	4.37	4.75	5.18
-p OH	5.50	5.52	5.50	5.52	5.80	7.17
-m CH_3	4.56	4.66	4.65	4.85	5.25	5.85
-p CH_3	4.94	4.80	4.76	4.80	5.12	6.24
-p OC_2H_5	5.25	5.31	5.32	5.41	5.48	6.69
-m OC_2H_5	4.13	4.08	4.08	4.17	4.28	4.69
-p OCH_3	5.29	5.23	5.19	5.17	5.48	5.73
(E) Pyridine series						
Nil	5.33	5.06	5.11	4.66	4.69	5.94
-m NH_2	5.98	6.02	5.94	5.85	5.97	7.38
-p NH_2	8.82	8.61	8.48	8.14	8.50	9.84
-p OH	4.82	4.80	4.87	4.87	5.08	6.39
-p DMA	5.11	5.14	5.06	4.99	5.18	6.50
-m C_2H_5	5.47	5.51	5.42	5.19	5.20	6.40
-p C_2H_5	5.77	5.81	5.75	5.51	5.43	6.67
-m CH_3	6.00	5.71	5.31	5.14	5.17	6.19
-p CH_3	6.17	5.92	5.68	5.39	5.50	6.61

plot was between 0.996 and 0.999. The ρ -values thus derived are given in Table 2.

The ρ -values increase with increase in the mol fraction of dioxane from 0.0 to 0.4. At dioxane mol fraction >0.4 , a reversal in this order is seen for benzoic acid and salicylic acid series and constancy for anilinium ion. The plots of ρ against $1/D$ or the mol fraction of dioxane do not exhibit a linear relationship over the entire range of composition. Decrease in dielectric constant should normally lead to increase in ρ -value due to change in the overall dielectric constant of the medium and/or due to specific solvation effect. If the ring solvation of the parent acid is unaffected in the substituted compounds, then, the plot of $pK(S)_s/pK(W)_s$ against $pK(S)_u/pK(W)_u$ should be linear with a unit slope¹⁴. Such plots were linear for $-CH_3$, ethyl and bromo substituted compounds but nonlinear for the $-NO_2$ and $-NH_2$ compounds. The deviation of the points from unit slope plot was greater at dioxane mol fraction of 0.24.

Application of Born equation

The ionization equilibria for the different series in mixed aqueous-solvents can be examined by the Born equation¹⁵

$$pK(S) - pK(W) = 121.6 (1/D - 0.0128) (1/r_{A^-} + 1/r_{H^+}) \dots (1)$$

In Eq. (1) $K(S)$ and $K(W)$ are the ionization constants of a neutral acid in a solvent mixture (S) and in water (W) respectively; D is the dielectric constant of the solvent mixture (S) and r_{A^-} and r_{H^+} represent the radii of the acid anion and the proton respectively. The radius of phenoxide and benzoate anions are assumed to be similar. The radius ($r_{A^-} = 3.31 \text{ \AA}$) of the phenoxide ion has been obtained from the volume (91.6 cm^3) of the

ion¹⁶. It was assumed that the molecule and its ion occupy an approximately equal spherical cavity in solution. r_{H^+} was taken equal to 0.80 \AA (ref. 17).

The variation of $pK(S) - pK(W)$ against $1/D$ predicted by Eq. (1) was compared with the experimental data for benzoic acid, phenol and salicylic acid and their substituted derivatives. The experimental points almost coincided with the theoretical line up to 40% of dioxane. Thereafter, these showed deviations which increased with the increase in dioxane content. All the experimental points taken together exhibit a curvature and do not confirm to the linear dependence required by the born equation¹⁵. The curved nature of these plots indicates the failure of the Born equation to take local variations in dielectric constant into account^{17,18}.

The non-applicability of this equation and the non-linearity of the plots is ascribed to the non-linear nature of the free energy function for the transfer of proton from water to water-dioxane mixtures¹⁹.

Variation of ρ with D

The values of $\Delta\rho (= \rho_s - \rho_w)$ were obtained for the five series and were averaged (Table 3). The standard deviations in 10, 20 and 40% dioxane-water mixtures are within the limits of uncertainties of these values, and are beyond the limits for 60% and 80% dioxane-water mixture. The $\Delta\rho$ for 90% was not averaged as the three values exhibited wide divergence. The almost constancy of $\Delta\rho$ for 10, 20 or 40% dioxane-water mixtures, for all the five series is worth noting because the ionization processes are different. The processes are ionogenic for phenol and benzoic acid series and isoelectric for pyridinium and anilinium ions.

$\Delta\rho$ varies linearly with $1/D$ (Fig. 1) except the one corresponding to 80% dioxane-water mixture

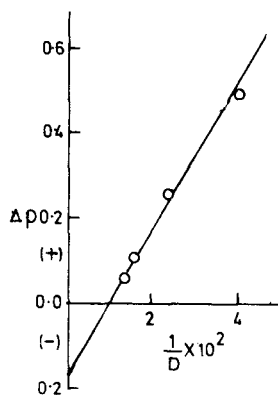
Table 2 — ρ -Values of Pyridinium and Anilinium Ions, Salicylic Acids, Benzoic Acids and Phenols in Various Dioxane-Water Medium at $303 \pm 0.1 \text{ K}$

% Dioxane (v/v)	Dielectric constant	Mol fraction of dioxane	ρ -Values				
			Pyridinium ion	Anilinium ion	Salicylic acid	Benzoic acid	Phenol
0	78.54	0.00	5.29 5.26*	2.94 2.93*	1.05	1.00 1.00*	2.23 2.26*
10	69.69	0.02	5.38	2.98	1.09	1.05	2.30
20	62.50	0.04	5.44	3.03	1.13	1.07	2.36
40	42.35	0.12	5.55	3.19	1.28	1.30	2.52
60	25.15	0.24	5.80	3.46	1.46	1.42	2.83
80	10.14	0.45	6.01	4.68	1.58	1.68	3.12
90	5.62	0.64		4.69	1.53	1.29	

*Literature values

Table 3— $\Delta\rho (\pm 0.03) (= \rho_w - \rho_s)$ Values of Pyridinium Ion, Salicylic Acids, Benzoic Acids and Phenols Series in Dioxane-Water Mixtures

% Dioxane (v/v)	$\Delta\rho$					Average $\Delta\rho$
	Pyridinium ion	Anilinium ion	Salicylic acid	Benzoic acid	Phenol	
10	0.09	0.04	0.04	0.05	0.07	0.06 \pm 0.02
20	0.15	0.09	0.08	0.07	0.13	0.104 \pm 0.03
40	0.26	0.25	0.23	0.30	0.29	0.266 \pm 0.03
60	0.51	0.52	0.41	0.42	0.60	0.492 \pm 0.07
80	0.72	0.74	0.53	0.68	0.89	0.705 \pm 0.138
90	—	0.75	0.48	0.29	—	—


 Fig. 1—Variation of $\Delta\rho$ with $1/D$, in water-dioxane mixtures

(correlation coefficient = 0.9992). The relationship between $\Delta\rho$ and $1/D$ obtained by the method of least squares is given by Eq. (2)

$$\Delta\rho = 19.34 (1/D) - 0.201 \quad \dots (2)$$

The utility and the scope of Eq. (2) was ascertained as follows:

(i) pK values for m - and p -substituted $-\text{CH}_3$, $-\text{Cl}$, $-\text{Br}$ and $-\text{OCH}_3$ anilinium ions were experimentally derived in alcohol-water mixtures. The data were utilized to get ρ_{expt} . ρ_{calc} was obtained from Eq. (2) and compared with ρ_{expt} . A satisfactory agreement was noted (Table 4).

(ii) Values of ρ_{calc} from Eq. (2) were compared with the literature ρ values for phenol, 4-nitrophenol and benzoic acid. A fairly satisfactory agreement is observed (Table 5) for all the mixtures, except the three, wherein the percentage of organic component is high.

(iii) The Hammett equation for the water medium (W) and solvent mixture (S) can be written separately (Eqs 3 and 4)

$$pK(W)_s = pK(W)_u - \rho_w \sigma \quad \dots (3)$$

$$pK(S)_s = pK(S)_u - \rho_s \sigma \quad \dots (4)$$

where s and u stand for substituted and unsubstituted derivatives respectively. Combining Eqs (3) and (4) we get

 Table 4—Hammett's ρ for Substituted Anilinium Ions in Different Alcohol-Water Mixtures at 303 ± 0.1 K

Alcohol	Dielectric constant	ρ -values	
		Obs.	Calc. from Eq. (2)
Methanol	74.1	2.98	2.99
Ethanol	59.0	3.03	3.07
Methanol	41.0	3.18	3.21
Ethanol	41.0	3.19	3.21
<i>n</i> -propanol	41.0	3.19	3.21

 Table 5—Comparison of ρ_{calc} from Eq. (2) with ρ_{lit} .

Medium	Dielectric constant	ρ -Values	
		Literature (refs 20-25)	Calc.
Benzoic acid			
50% methanol	54.9	1.09	1.15
Pure methanol	31.5	1.54	1.41*
70% ethanol	38.0	1.74	1.31*
50% methanol	54.9	1.24	1.15
4-Substituted phenols			
10% methanol	74.1	2.29	2.29
40% methanol	59.6	2.45	2.38
50% methanol	54.9	2.46	2.38
60% methanol	50.1	2.48	2.42
80% methanol	40.0	2.42	2.51
90% methanol	35.7	2.36	2.57*
Phenol			
Butanol-water	70.0	2.34	2.31

tuted derivatives respectively. Combining Eqs (3) and (4) we get

$$pK(S)_s = \frac{\rho_s}{\rho_w} \{pK(W)_s - pK(W)_u\} + pK(S)_u \quad \dots (5)$$

The magnitude of ρ_s for any solvent mixture with a known dielectric constant can be derived from Eq. (2). Values of $pK(W)_u$ and $pK(W)_s$ for

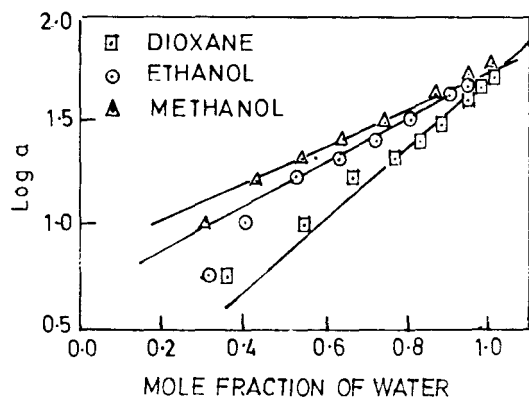
Table 6—Comparison of pK Values Observed by Other Workers with the Ones Calculated by the JAK Equation

	Ethanol		
4-t-butylpyridine	40	4.86	4.98
3-CH ₃ -aniline	50	4.09	4.09
3,5-dimethylaniline	50	4.61	4.59
	Methanol		
4-Nitrophenol	10	7.18	7.18
	20	7.31	7.28
	30	7.44	7.50
	40	7.57	7.63
	50	7.72	7.78
	60	7.91	7.94
	70	8.14	8.14
	80	8.47	8.36
4-Methylphenol	90	9.07	8.80
	20	10.57	10.58
	30	10.81	10.82
	40	11.01	11.06
	50	11.19	11.26
	60	11.34	11.38

common organic acids are available in the literature¹². The $pK(S)_s$ for any substituted compound in any solvent mixture, therefore, can be obtained from Eq. (5), provided $pK(S)_u$ is known. $pK(S)_s$ values thus obtained for substituted anilines and phenols are given in Table 6. The agreement between the calculated and the literature values is fairly close for all the solvent mixtures, except those having higher percentage (>70%) of organic component. Equation (2) therefore seems to be capable of predicting pK values of an organic acid in a solvent mixture where the organic part is not rich.

In aquo organic solvent mixture the two components differ in their solvating power. Hence activity of water is a principal deciding factor for pK .

The linear variation of pK with the mol fraction of organic component in aquo organic solvent


 Fig. 2—Plot of $\log a_w$ against mol fraction of the water in mixed aqueous solvents

mixture requires that the water activity be proportional to the mol fraction of water in the solvent mixture. The plots of $\log a_w$ versus mol fraction of water for the three binary solvent mixtures are shown in Fig. 2. For each mixture, the points corresponding to mixtures having mol fraction of water greater than 0.6 only, fall on a straight line.

It seems, therefore, that the dielectric constant of a medium as well as the mol fraction of water, are the two factors responsible for the dissociation equilibria. This clearly accounts for the limited linearity in pK versus $1/D$ plots and the limited validity of Eq. (2).

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