As observed, potassium salts are more dissociated than sodium salts. The pK values of the nitrates and halides of sodium and potassium in any solvent composition are found to decrease in the order: $NO_3^- > Cl^- > I^- > Br^-$ which is reverse to that of their conductivities. In other words, higher the conductivity values greater the dissociation.

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THERMODYNAMICS OF DISSOCIATION OF BENZOIC ACIDS IN MIXED SOLVENTS

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Free energies of transfer of ortho-, meta-, and para substituted nitro-, chloro-, hydroxy- and amino benzoic acids from water to binary solvent mixtures have been estimated from pK_a data of the acids obtained from pH measurements. In addition, the effect of substituents of the pK_a value of benzoic acid has been discussed in these binary solvents in terms of qualitative theory of substituent effects. Linear free energy relationships have been examined in the mixed solvents.

Studies on the dissociation constants of acids and especially substituted benzoic acids in aqueous [1] and a few non-aqueous media, eg., formamide [2] ethylene glycol [3] propylene glycol [3], ethanol [3] and tetrahydrofuran [3] have received much attention. Thermodyanamics of dissociation of a number of mono-, and dicarboxylic acids in a wide variety of mixed solvents [4] are reported. However knowledge of the thermodynamic data in mixed solvents is still lacking. Such studies are helpful in understanding the solvent effects, solute-solvent, solvent-solvent interactions on the thermodynamics parameters.

In this communication we report the studies of ortho-, meta-, and para substituted nitro-, chloro-, hydroxy-, and amino benzoic acids in different methanol-, ethanol-, 1-propanol, 2-propanol-, glycerol-, d-glucose-, and d-fructose-water mixtures at 25°C and the corresponding free energy changes calculated from pK_a values.

EXPERIMENTAL

Methanol, ethanol, 1-propanol, 2-propanol and glycerol were B.D.H., Laboratory reagents and purified by methods described in earlier

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communications [5]. d-Glucose and d-fructose (E. Merck, G.R.) were used as such. Solvent of various compositions were made up by weight in conductivity water. Benzoic and mononitro benzoic acids were the same samples as used earlier [6]. Chloro-, hydroxy-, and amino benzoic acids were either of G.R samples or B.D.H Laboratory reagents and purified by the methods available in the literature[7]. Potassium salts of these acids were prepared by the method similar to that described elsewhere[8].

Solutions for pH measurements were prepared by dissolving the appropriate weighed amounts of acids and salts in known volumes of mixed solvents. Potassium chloride (G.R.) was used to maintain the ionic strength of the solutions. Solutions of very low ionic strength (1×10^{-3} - 8×10^{-4} M) were used.

The pH measurements were carried out with a Systronic pH Meter type 324. The pH meter was standardised against aqueous buffers of known pH at the required temperature. The correction of pH measurements in the mixed solvents was made by following the Van Uitert and Hass [9] method of taking pH meter readings on a series of solutions containing HCl and KCl in different solvents starting from pure water to various mixed solvents and converting to hydrogen ion concentration by the usual expression [9]. All solutions are thermostated at $25 \pm 0.05^{\circ}$C and de-oxygenated by bubbling of N_2 gas.

RESULTS AND DISCUSSION

The thermodynamic acid dissociation constant, K_{am}(molal scale) for the reaction, namely

$$HA + \text{solvent} \rightleftharpoons H^+(\text{solvated}) + A^-(\text{solvated})$$

is given by

$$K_{am} = \frac{m_{H^+} \cdot m_{A^-}}{m_{HA}} \cdot \frac{\gamma_{H^+} \cdot \gamma_{A^-}}{\gamma_{HA}} \qquad \ldots(1)$$

where m and γ's are the molalities and activity co-efficients, repectively, of the species designated. The molar concentrations of the acid and salt solutions were converted into the molal scale using the density values (d_o) of the solvents concerned. Assuming γ_{HA} equals unity, neglecting salt effects on the neutral molecule, equation (1) becomes,

$$K_{am} = \frac{m_{H^+} \; m_{A^-}}{m_{HA}} \cdot \gamma_{\pm}^2 \qquad (2)$$

where $\gamma_{\pm}$ is the mean molal activity coefficient. Making appropriate corrections of the hydrogen ion molality from the pH meter readings of the solutions each containing an acid, HA (m_1), the potassium salt of that acid, KA (m_2) and an inert electrolyte, KCl (m_3) in various solvents by Van Uitert and Haas method and using the Debye-Huckel limiting equation for the mean molal activity coefficient, the dissociation constant is given by [4]

$$-\log K_{am} = \log \frac{(m_1 - m_{H^+})}{m_{H^+}(m_2 + m_{H^+})} + 2A\sqrt{\mu d_o} \qquad (3)$$

The ionic strength, μ is given by, $\mu = m_{H^+} + m_2 + m_3$. The Debye-Huckel constant, A for different solvents was either obtained from the literature or calculated using the dielectric constant of the solvents [10] in the appropriate equation. The R.H.S. of equation (3) was calculated from the experimental data for every ionic strength of the solution and the linear extrapolation to $\mu = 0$ yielded the thermodynamic dissociation constant at zero ionic strength. The values of $-\log K_{am}$ (i.e., pK_{am}) thus obtained are listed in Table 1 for different acids in various solvents together with similar data in water [1] and mixed solvents [5] for the sake of comparison.

The standard gibbs free energy change, ΔG°_m for the dissociation process of the acid has been computed at 25°C from the equation,

$$\Delta G^{\circ}_m = 2.3026 \; RT \; pK_{am} \qquad (4)$$

The standard Gibbs free energy change (mole-fraction scale) for the transfer process associated with the dissociation of acids between water (w) and mixed solvents (s) of various compositions have been evaluated from

$$G^{\circ}_{Nt} = 2.3036 \; RT \; [(pK_{aN})_S - (pK_{aN})_W] \qquad (5)$$

where $pK_{aN} = pK_{am} + 2 \log (1000/\bar{M})$ and M is the average molecular weight of the solvent concerned. ΔG°_t is expressed in mole-fraction scale in order to eliminate any change due to concentration change. The values of ΔG°_m and ΔG°_{Nt} are listed in Table 2.

A comparison of our results with those of other workers in the mixed solvents is not possible because of lack of data in the present compositions of the mixed solvents in this study. However, the pK_a values of benzoic, salicyclic and meta-chloro benzoic

acids reported in 8 & 16 wt% methanol-water mixtures at 25° C from conductance measurement [11] show that the present set of data in 10 and 20 wt % methanol-water mixtures seems to be slightly higher compared to conductometric data. It is often seen that different physical methods used for the determination of pK_a value give slightly different values [12,13]. So such differences between the results obtained by different physical methods are not unusual; examples are plentiful in the literature [14]. Considering the limitations of the pH measurements in aqueo-organic solvent systems, the results obtained in the present study certainly seem to be quite trustworthy and in order in various mixed solvents.

As observed from Table 1, pK_a values are higher in the mixed solvents compared to those in water and tend to increase with the increasing organic solvent content as expected. Figure 1 indicates the nature of the plot of pK against the reciprocal of the dielectric constant (D^{-1}) of aqueo-organic solvents for all the thirteen acids studied in the present investigation. Barring a few exceptions, pK_a values are found to increase with decrease in dielectric constant (i.e., increase of D^{-1}) of the aqueo-organic solvents.

The higher pK_a values of benzoic and nitrobenzoic acids in 30 wt% d-glucose and 20 wt% ethanol than in 20 wt% methanol and 20 wt% 1-propanol, respectively, may be explained as due to the preferential solvation of uncharged acids by the corresponding organic solvent molecules. Similar deviations are observed for para -chloro and meta-hydroxy benzoic acids in 20 wt% ethanol and 2-propanol solvents. However, the relative strengths of the acids in the mixed solvents are found to be the same as that in aqueous medium. The effect of substituents on the dissociation process of the carboxylic group in these mixed solvents appears to be in complete agreement with the qualitative theory of substituent effects.

The dissociation constants of the benzoic acids in different mixed solvents were correlated by the 'σ' (substituent constant) values by means of the Hammett equation [15]. Using the best 'σ' values available in the literature [16], the Hammett reaction constant, ρ obtained from the slope of the plot of log K_a^x / K_a^o

TABLE 1

VALUES* OF pK_{am} FOR BENZOIC AND SUBSTITUTED BENZOIC ACIDS IN [1(b),5] AND MIXED SOLVENTS AT 25°C

Acid	Wt%	Parent	o-NO_2	m-NO_2	p-NO_2	p-Cl	m-Cl	p-Cl	p-OH	m-OH	p-OH	o-NH_2	m-NH_2	p-NH_2
	0	4.29	2.12	3.63	3.32	3.19	3.70	3.85	2.89	4.14	4.60	4.99	4.80	4.92
methanol	10	4.50	3.79	4.39	3.99	4.36	4.40	4.45	3.40	4.47	4.88	5.55	5.38	5.47
	20	4.59	3.87	4.46	4.15	4.48	4.52	4.56	3.52	4.58	5.17	5.86	5.69	5.79
Ethanol	10	4.55	3.84	4.43	4.11	4.43	4.46	4.51	3.41	4.53	4.96	5.67	5.49	5.59
	20	4.68	4.11	4.64	4.35	4.52	4.61	4.66	3.54	4.63	5.20	5.89	5.74	5.83
1-Propanol	10	4.57	3.87	4.45	4.14	4.46	4.51	4.54	3.45	4.55	5.02	5.74	5.58	5.69
	20	4.61	3.89	4.47	4.17	4.53	4.58	4.60	3.57	4.59	5.22	5.94	5.81	5.89
2-Propanol	10	4.58	3.89	4.46	4.16	4.48	4.51	4.56	3.43	4.54	5.08	5.79	5.63	5.72
	20	4.62	3.91	4.49	4.20	4.55	4.59	4.61	3.59	4.79	5.96	5.99	5.86	5.94
Gycerol	5	4.42	3.68	4.29	3.85	4.16	4.28	4.39	3.23	4.56	4.88	5.29	5.13	5.21
	10	4.47	3.76	4.38	3.93	4.31	4.37	4.44	3.49	4.63	5.03	5.45	5.29	5.38
	5	4.39	3.38	4.06	3.55	4.08	4.21	4.36	3.21	4.50	4.82	5.18	5.01	5.11
D-Glucose	10	4.44	3.70	4.32	3.88	4.25	4.33	4.41	3.47	4.61	4.87	5.38	5.22	5.32
	20	4.52	3.80	4.41	4.08	4.38	4.41	4.47	3.51	4.70	5.01	5.60	5.43	5.51
	30	4.65	4.11	4.61	4.36	4.52	4.59	4.63	3.55	4.80	5.12	5.82	5.67	5.74
D-Fructose	5	4.45	3.44	4.09	3.62	4.11	4.18	4.35	3.29	4.52	4.83	5.21	5.05	5.15
	10	4.50	3.78	4.42	3.94	4.27	4.35	4.42	3.49	4.60	4.88	5.40	5.24	5.34

* Uncertainties $pK_{am} = \pm$ 0.02 to 0.05 log units

TABLE 2

VALUES* OF ΔG°_{m} (a) AND ΔG°_{Nt} (b) FOR THE DISSOCIATION OF BENZOIC AND SUBSTITUTED BENZOIC ACIDS IN WATER AND MIXED SOLVENTS AT 25°C (ΔG° in KJ/mole)

Acid / Solvent	Wt%	Parent		o-NO_2		m-NO_2		p-NO_2		o-Cl		m-Cl		p-Cl	
		a	b	a	b	a	b	a	b	a	b	a	b	a	b
Methanol	0	23.98	-	11.73	-	19.93	-	18.26	-	18.31	-	21.24	-	21.96	-
	10	25.68	1.47	21.62	9.67	25.05	4.92	22.77	4.28	24.88	6.35	25.10	3.64	25.39	3.21
	20	26.19	1.75	22.08	9.90	25.45	5.06	23.68	4.96	25.56	6.80	25.79	4.10	26.02	3.60
Ethanol	10	25.96	1.67	21.91	9.87	25.28	5.04	23.45	4.88	25.28	6.66	25.45	3.90	25.73	3.46
	20	26.70	2.08	23.45	11.08	26.47	5.90	24.82	5.92	25.79	6.84	26.30	4.42	26.59	3.99
1-Propanol	10	26.07	1.73	22.08	9.99	25.39	5.10	23.62	5.00	25.45	6.78	25.73	4.13	25.90	3.58
	20	26.30	1.57	22.19	9.72	25.50	4.83	23.79	4.79	25.85	6.79	26.26	4.14	26.25	3.54
2-Propanol	10	26.13	1.79	22.19	10.11	25.45	5.16	23.74	5.12	25.56	6.89	25.73	4.13	26.02	3.70
	20	26.36	1.63	22.31	9.83	25.62	4.94	23.96	4.96	25.96	6.90	26.19	4.20	26.30	3.60
Glycerol	5	25.22	1.03	21.00	9.06	24.48	4.34	21.97	3.50	23.74	5.22	24.42	2.98	25.05	2.88
	10	25.50	1.11	21.45	9.31	24.99	4.65	22.42	3.75	24.59	5.87	24.93	3.28	25.33	2.96
D-Glucose	5	25.05	0.84	19.29	7.33	23.16	3.01	20.26	1.77	23.28	4.74	24.02	2.55	24.88	2.69
	10	25.33	0.88	21.11	8.91	24.65	4.25	22.14	3.41	24.25	5.47	24.71	3.00	25.16	2.73
	20	25.79	0.82	21.68	8.97	25.16	4.25	23.28	4.04	24.99	5.70	25.16	2.94	25.50	2.56
	30	26.53	0.99	23.45	10.16	26.30	4.81	24.88	5.06	25.79	5.92	26.19	3.39	26.42	2.90
D-Fructose	5	25.39	1.18	19.63	7.67	23.34	3.18	20.65	2.17	23.45	4.91	23.85	2.38	24.82	2.63
	10	25.68	1.22	21.57	9.37	25.22	4.82	22.48	3.75	24.36	5.58	24.82	3.11	25.22	2.79

Acid / Solvent	Wt%	o-OH		m-OH		p-OH		o-NH_2		m-NH_2		p-NH_2	
		a	b	a	b	a	b	a	b	a	b	a	b
Methanol	0	16.49	-	23.58	-	26.23	-	28.45	-	27.40	-	28.06	-
	10	19.40	2.69	25.50	1.70	27.84	1.39	31.67	2.99	30.70	3.08	31.21	2.93
	20	20.08	3.14	26.13	2.10	29.50	2.81	33.34	4.53	32.46	4.61	33.04	4.52
Ethanol	10	19.46	2.66	25.85	1.96	28.30	1.76	32.35	3.59	31.32	3.61	31.89	3.53
	20	20.20	3.07	26.82	2.19	29.67	3.08	33.61	4.51	32.75	4.71	33.26	4.56
1-Propanol	10	19.68	2.83	25.96	2.02	28.64	2.05	32.75	3.94	31.84	4.08	32.46	4.04
	20	20.37	3.13	26.19	1.86	29.78	3.15	33.89	4.69	33.15	5.00	33.61	4.80
2-Propanol	10	19.57	2.72	25.90	1.96	28.98	2.40	33.04	4.23	32.12	4.36	32.64	4.22
	20	20.48	3.24	27.33	3.00	30.01	3.32	34.18	4.98	33.43	5.29	33.89	5.08
Glycerol	5	18.43	1.74	26.02	2.24	27.84	1.41	30.18	1.53	29.27	1.67	29.73	1.47
	10	19.91	3.01	26.42	2.43	28.70	2.06	31.10	2.23	30.18	2.37	30.70	2.22
D-Glucose	5	18.32	1.60	25.67	1.86	27.50	1.04	29.56	0.88	28.59	0.96	29.16	0.87
	10	19.80	2.84	26.20	2.25	27.79	1.09	30.70	1.78	29.78	1.92	30.35	1.83
	20	20.03	2.56	26.82	2.76	28.58	1.37	31.95	2.52	30.98	2.60	31.44	2.39
	30	20.25	2.20	27.39	2.25	29.21	1.42	33.21	3.20	32.35	3.39	32.75	3.13
D-Fructose	5	18.77	2.05	25.79	1.98	27.56	1.10	29.73	1.05	28.81	1.19	29.38	1.10
	10	19.91	2.95	26.25	2.20	27.84	1.14	30.81	1.89	29.90	2.03	30.47	1.94

* Uncertainties ΔG°_{m} # ± 28J in ΔG°_{Nt} = ± 5 J

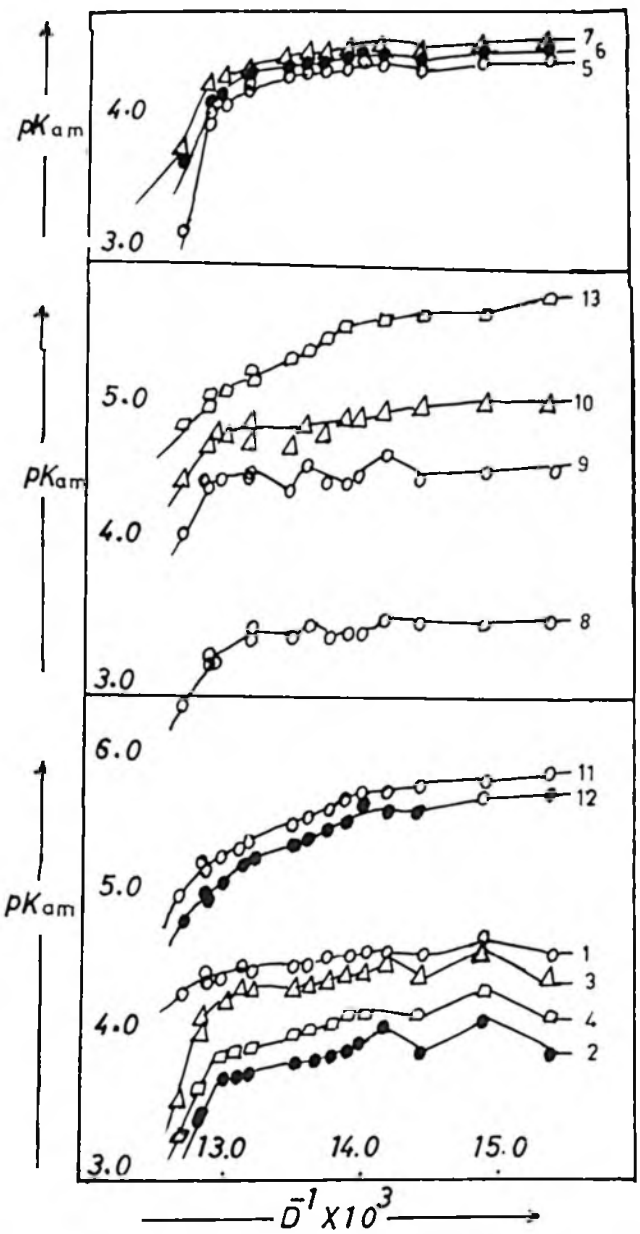


Fig. 1 Variation of pK_{am} of benzoic and substituted benzoic acids with reciprocal of dielectric constants of mixed solvents
1. Benzoic, 2. O-Nitro, 3. m-Nitro, 4. p-Nitro, 5. O-Chloro, 6. m-Chloro, 7. p-Chioro, 8. O-Hydroxy, 9.m-Hydroxy 10. p-Hydroxy, 11. o-Amino, 12.m-Amino 13. p-Amino benzoic acid

against σ in various mixed solvents, where K_a^o is the dissociation constant of benzoic acid and K_a^x is the corresponding constant of substitued benzoic acid carrying substituent, X, are recoreded in Table 3 along with those reported in water, methanol and ethanol [17]. The ρ values are found to be positive in all the solvents but less in the mixed solvents as compared to that in the corresponding non-aqueous solvents. As observed, ρ increased with increasing the organic solvent content (except in 5 wt% d-glucose and 5 wt% d-fructose) in water. Deviations observed in cases of 5 wt% d-glucose and 5 wt% d-fructose are, however, indicative of the fact that the change of solvent not only affects ρ but also the effect of substituents to some extent. The ρ value provides a measure of the sensitivity of the reaction to the basicity of the acid (pK_a) and depends on the electron attracting power of the substituents in the solvent. The effects of the structural variation and ionic solvation in the solvents concerned are apparent from the Hammett plot. The increase in ρ accompanying a decrease in the ion-solvating power and dielectric constant of the solvent that may be seen in comparing the dissociation of benzoic acids in water, methanol and ethanol and in different compositions of the aqueo-organic solvent mixtures is commonly found. The stronger electrostatic interaction between the substituents and the reaction centre in a solvent of lower dielectric constant is reflected in a high ρ value in 20 wt% 2-propanol indicating a low degree of proton transfer (i.e, high pK_a value) whereas a low ρ value indicating a high degree of proton transfer (i.e., low pK_a value) in 5 wt% glycerol having higher dielectric constant amply supports the view that electrostatic interaction between the substituents and the reaction centre is weaker in a medium of higher dielectric constant. Deviations from this contention, however, may be explained as pointed out earlier due to the preferential solvation of uncharged acids by the corresponding organic solvent molecules.

Using the ionic radii for the hydrogen (γ_H) and carboxylate ions (γ_A), it is possible to estimate the approximate difference of pK values in mixed solvents from Born equation [18].

$$\Delta pK_a = (spK_a - wpK_a) = 121.6 \left(\frac{1}{D_s} - \frac{1}{D_w}\right)\left(\gamma_H^{-1} + \gamma_A^{-1}\right)$$

and corrlated quantitavely with the experimental data. As observed, the experiment ΔpK_a values in the mixed solvents do not agree with that computed from Born equation. Similar discrepency has been reported on benzoic acids in methanol-water mixtures [11]. The uncertain values of ionic radii, approximate nature of the Born equation, solute-solvent interactions and solvent basicity of uncertain magnitude may be the plausible cause of such disagreement. Deviations are apparent because of the non-electrostatic part as being the result of

TABLE 3

ρ VALUES OF (HAMMETT REACTION CONSTANT) FOR BENZOIC IN VARIOUS SOLVENTS AT 25° C

wt% organic solvent										
Methanol				Ethanol			1-Propanol		2-Proponal	
0 [17]	10	20	100 [17]	10	20	100 [17]	10	20	10	20
1.000	0.877	1.041	1.537	0.906	0.938	1.957	0.925	1.100	0.980	1.122
Glycerol				D-Glucose			D-Fructose			
5		10		5	10	20	30	5	10	
0.826		0.913		0.918	0.882	0.889	0.903	0.914	0.837	

mainly ion-solvent and solvent-solvent interactions in the mixed solvents. Thus the overall variation of ΔpK_a with solvent composition indicates the significant role of specific solute-solvent interactions.

A perusal of Table 2 shows that the ΔG°_{Nt} values for the transfer from water to the mixed solvent are positive and increase (except for benzoic, and nitro benzoic acids in 20 wt% 1-propanol, benzoic, meta nitro-, meta chloro-, para cloro-, and para hydroxy benzoic acids in 20 wt% d-glucose) with increasing proportion of organic co-solvents in the mixture. The increased ΔG°_{Nt} values indicate that the acids have more energy in the mixed media than in water, and hence the transfer process for the acids from water to the mixed solvent is not favourable.

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