Conductometric Determination of Thermodynamics Dissociation Constants of Benzoic and Nitrobenzoic Acid in Methanol-Water Mixtures at 298 K

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The thermodynamic dissociation constants and the limiting molar conductivities of 2-, 3-, 4-nitrobenzoic and benzoic acids have been determined in water-methanol mixtures at 298 K. The experimental data are analyzed with the Lee and Wheaton conductance equation incorporating modifications. The derived results are compared with the ones in literature, pertaining to analogous media. The findings are interpreted in terms of solute-solvent interactions, intramolecular hydrogen bonding, resonance and inductive effect and the substituent position. The study showed that the dissociation order decreases as 2-nitrobenzoic acid> 3-nitrobenzoic acid≈ 4-nitro benzoic acid> benzoic acid.

Protonation/deprotonation equilibria leading to the study of acid-base equilibria have been under investigation in pure and mixed solvents since many years. The ionization constant of an acid is largely influenced mostly by the structure of the acid but also by the nature of the solvent.[1-4] Potentiometric and spectrophotometric techniques are quite popular for obtaining dissociation constants of acids and bases.[5-7] However, the ionization of acids in methanol-water (MeOH-H_2O) mixtures varies with solvent composition in a manner which is still not completely understood.[8,9] In contranst to potentiometry, the conductimetry provides a simple and accurate method for the determination of dissociation constants of acids without any primary and secondary buffer solutions required for calibration of the platinum electrode.[10-12]

In this paper the conductance behavior of 2-, 3-, 4-nitrobenzoic acids along with benzoic acid (as a model compound) in MeOH-H_2O mixtures at 298 K is examined. The pK_a values (thermodynamic dissociation constants) are derived from conductance data using the Lee and Wheaton conductance equation (in series form) incorporating modifications.[13,14] Finished results are compared with those by other workers pertaining to the same and similar acids in analogous media.

Experimental

Benzoic and nitrobenzoic acids used in the present work were Merck products of ultrahigh purity. They were crystallized twice from ethanol-water mixtures, dried under vacuum over P_2O_5 and stored in a desiccator.

Methanol (Analar BDH) was distilled over sulfanilic acid and the middle fraction was collected for use. The deionized conductivity water (triply distilled) was used as an aqueous medium and for preparation of MeOH-H_2O mixtures (w/w composition). The purity of solvents was checked from their physical parameters such as density, viscosity, and dielectric constant at 298 K.

The conductance measurements were made in the same way as described elsewhere.[15,16] An Orion Research conductivity meter model 101, was used for the purpose. Two platinized platinum electrodes (cell constants: 0.857 and 1.151 cm^{-1}) were used. The temperature of water baths was controlled at 25±0.01 °C. No appreciable variations in conductance were observed in changing frequency range from 80 Hz to 3 kHz. Duplicate measurements for each mixture were made, the results varied within±0.1% only.

Viscosities, densities, and dielectric constants of various mixtures were measured in the same way as described earlier,[17] which have been found in good agreement with the values cited in literature.[18]

Results

Physical properties of MeOH-H_2O mixtures are listed in Table 1. The corresponding values of the molar conductances are given in Table 2 for all the four acids in solvent mixtures of different composition listed therein. The experimental data were analyzed with the Lee and Wheaton conductance equation in its series form.[13,14] The selection of the equation was tentative since it was based on a model warranting the study of the dissociation process and short range interactions closely. The limiting molar conductance (Λ_0) and association constant (K_A) for the process [$H^+ + A^- \overset{K_A}{\rightleftarrows} H^+A^-$] were deduced from the equations:

$$\Lambda = \gamma[\Lambda_0(1+\Delta X/X) - \Delta\Lambda_{el}] \qquad (1)$$

$$K_A = (1-\gamma)/\gamma^2 f^2 c \qquad (2)$$

$$-\ln f = bk/2(1+kR),\ b = e^2/DKT \qquad (3)$$

for Λ_0 and K_A values which minimize

$$\sigma_\Lambda = \sum_j [\Lambda_j(\text{cal}) - \Lambda_j(\text{obs})]^2/n-2 \qquad (4)$$

Table 1. Physical Properties of MeOH-H_2O Mixtures at 298 K

% MeOH (w/w)	ρ / $g\cdot cm^{-3}$	η / $cP^{a)}$	D
0	0.9971	0.890	78.65
10	0.9806	1.153	74.23
30	0.9437	1.581	63.93
50	0.9129	1.545	55.17
70	0.8481	1.215	37.88

ρ=density; η=viscosity; D=dielectric constant.
a) 1 cP=10^{-3} Pa s.

The symbols have their usual significance. The study revealed that in the case of carboxylic acids no minimum is observed in a R-σ_A (%) plot. The value of distance parameter R was set equal to $2b$ as suggested by Fuoss.[22] The derived conductance parameters are given in Table 3.

From the K_A values, the respective pK_a (i.e. dissociation constant) values were calculated using the relationship:

$$pK_a = -\log K_d = -\log (1/K_A) \qquad (5)$$

Values of pK_a for benzoic and nitrobenzoic acids at 298 K are presented in Table 4. The solvent effect of MeOH on the dissociation of these acids is shown in Fig. 2, where the difference between pK_a^s (the value of pK_a in the fixed solvent-mixture) and pK_a^w (the value of pK_a in water) is plotted as a function x, the mole fraction of MeOH in methanol-water mixtures. The

Table 2. Molar Conductances of Solutions of Acids in MeOH-H_2O Mixtures at 298 K

Wt. % MeOH	0	10	30	50	70
10^4C	Λ	Λ	Λ	Λ	Λ
$mol \cdot dm^{-3}$	$S \cdot cm^2 \cdot mol^{-1}$	$S \cdot cm^2 \cdot mol^{-1}$	$S \cdot cm^2 \cdot mol^{-1}$	$S \cdot cm^2 \cdot mol^{-1}$	$S \cdot cm^2 \cdot mol^{-1}$
		Benzoic acid			
1.961	168.13	82.42	42.39	21.36	9.55
5.660	111.05	52.42	26.28	12.91	5.75
9.091	90.71	42.41	21.08	10.27	4.56
12.281	79.55	37.00	18.29	8.88	3.94
12.254	72.21	33.46	16.51	7.98	3.54
18.033	67.01	31.20	15.24	7.36	3.27
20.635	63.04	29.08	14.29	6.89	3.06
23.077	59.91	27.59	13.56	6.53	2.90
25.373	57.39	26.40	12.94	6.23	2.77
27.536	55.30	25.39	12.44	5.98	2.65
		2-Nitrobenzoic acid			
1.961	390.87	268.37	176.45	92.27	46.92
5.660	374.92	251.64	153.99	69.65	30.31
9.091	362.57	239.50	140.53	59.67	24.64
12.281	352.57	230.11	131.24	53.68	21.54
15.254	344.21	222.55	124.32	49.57	19.52
18.033	337.13	216.30	118.91	46.54	18.09
20.635	330.99	211.02	114.53	44.20	17.01
23.077	325.63	206.48	110.89	42.30	16.15
25.373	320.89	202.54	107.81	40.75	15.46
27.536	316.67	199.03	105.03	39.86	14.88
		3-Nitrobenzoic acid			
1.961	292.95	207.85	114.65	50.81	25.88
5.660	220.80	155.55	79.61	33.82	16.13
9.091	188.95	132.75	66.22	27.73	12.71
12.281	169.82	119.15	58.60	24.36	10.93
15.254	156.71	109.84	53.54	22.15	9.87
10.033	147.05	103.01	49.88	20.57	9.15
20.635	139.54	97.71	47.09	19.37	8.53
23.077	133.53	93.46	44.87	18.42	8.10
25.373	128.56	89.96	43.05	17.65	7.72
27.536	124.34	86.99	41.52	16.99	7.43

Wt. % MeOH	0	10		30	
10^4C	Λ	10^4C	Λ	10^4C	Λ
$mol \cdot dm^{-3}$	$S \cdot cm^2 \cdot mol^{-1}$	$mol \cdot dm^{-3}$	$S \cdot cm^2 \cdot mol^{-1}$	$mol \cdot dm^{-3}$	$S \cdot cm^2 \cdot mol^{-1}$
		4-Nitrobenzoic acid			
1.48	296.75	1.481	249.87	1.081	166.57
3.871	233.25	3.871	197.06	2.927	124.46
5.714	212.89	5.714	174.95	4.444	107.61
7.179	191.39	7.179	162.27	5.714	98.12
8.377	181.40	8.373	153.87	6.772	91.89
9.362	174.33	9.362	148.04	7.719	87.44
10.196	169.01	9.795	145.67	8.525	84.10
10.566	166.82	10.196	143.36	8.888	82.73
10.909	164.87	10.568	140.82	9.231	81.50

Table 2. (Continued)

50		70	
10^4C	Λ	10^4C	Λ
$mol\cdot dm^{-3}$	$S\cdot cm^2\cdot mol^{-1}$	$mol\cdot dm^{-3}$	$S\cdot cm^2\cdot mol^{-1}$
1.481	73.89	1.961	26.47
3.871	51.24	5.660	16.23
5.714	45.48	9.091	12.96
7.179	39.58	12.281	11.19
8.373	37.07	15.259	10.06
9.362	25.31	18.033	9.29
10.196	33.02	20.635	8.72
10.566	33.49	21.675	8.48
10.909	33.03	23.077	8.26

Table 3. Conductance Parameters of Acids in MeOH-H_2O Mixtures at 298 K

% MeOH w/w	Λ_0 $S\cdot cm^2\cdot mol^{-1}$	σ %	K_A $dm^3\cdot mol^{-1}$
	Benzoic acid		
0	393.08	0.084	16635
10	262.16	0.028	20700
30	197.77	0.031	87625
50	190.94	0.011	366481
70	105.44	0.008	1574078
	2-Nitrobenzoic acid		
0	402.08	0.032	125
10	280.43	0.051	214
30	196.24	0.057	620
50	128.83	0.017	2830
70	133.55	0.035	27432
	3-Nitrobenzoic acid		
0	408.73	0.012	2834
10	295.17	0.008	3091
30	206.97	0.013	7534
50	144.67	0.003	14708
70	161.49	0.031	170260
	4-Nitrobenzoic acid		
0	376.54	0.049	2785
10	336.95	0.008	3712
30	251.82	0.010	7235
50	169.44	0.040	20123
70	173.82	0.021	189459

Table 4. pK_a Values and Difference of Standard Molar Gibbs Energy of Transfer $\Delta_{tr}G^\circ_m$ at 298 K of Acids for Water to Methanol-Water

% MeOH (w/w) Acid	0	10	30	50	70
	pK_avalues				
Benzoic	4.22	4.31	4.94	5.56	6.20
2-Nitrobenzoic	2.10	2.33	2.79	3.45	4.44
3-Nitrobenzoic	3.45	3.49	3.88	4.17	5.23
4-Nitrobenzoic	3.45	3.50	3.86	4.30	5.27
	$\Delta_{tr}G^\circ_m/kJ\cdot mol^{-1}$				
Benzoic		0.51	2.97	7.65	11.30
2-Nitrobenzoic		1.31	3.94	7.70	13.35
3-Nitrobenzoic		0.23	2.45	4.11	10.16
4-Nitrobenzoic		0.29	2.34	4.85	10.39

observed changes of pK^s_a and standard molar Gibbs free energy of transfer $\Delta_{tr}G^\circ_m$ were calculated from:

$$\Delta_{tr}G^\circ_m = -RT \ln 10 \Delta pK_a = 5.707\ [pK^s_a - pK^w_a]\ kJ\cdot mol^{-1} \qquad (6)$$

and are presented in Table 4.

Discussion

The pK_a values of benzoic and 2-, 3-, and 4-nitrobenzoic acids in aqueous medium are in good agreement with those quoted in literature, mainly derived by potentiometric and some other methods.[23] The dissociation study of benzoic and the nitrobenzoic acid in alcohol-water mixtures is available in literature.[1,19—21] The present pK_a values for benzoic acid (in some MeOH-H_2O mixtures) are in good agreement with previous study in Fig. 1. In this figure, the derived results are compared with those by Lahiri et al.[19] for 4-nitrobenzoic acid in MeOH-H_2O mixtures. As is obvious, their pK_a values in 8—60 wt% MeOH-H_2O mixtures are higher than our derived values. This could be attributed to their so called corrections in pH values of acidic solutions in binary solvent mixtures. Also, procedural digression from the normal potentiometric method for determination of pK_a values of carboxylic acids in mixed solvent systems could also be another cause for this effect.[1,4] On similar ground, the present results do not agree with those derived by Dash et al.[21] who undertook potentiometric calibration with reference to aqueous phase. Therefore, a direct comparison with their results could be oversimplification of actual situation.

The solvent effect on the dissociation of these acids is shown in Fig. 2. The plots of pK_a vs. mole fraction x of methanolic contents in MeOH-H_2O mixtures are not linear. A similar behavior of these acids in pK_a vs. $(1/D_s - 1/D_w)$ plots, may also be observed, where D_s and D_w are dielectric constants of mixtures and water, respectively. If only electrostatic interactions among the ions would have been operational these plots should have been linear, detailed by Born.[24] The present investigation thus suggest that in case of nitrobenzoic acids a nonelectrostatic part of the standard free

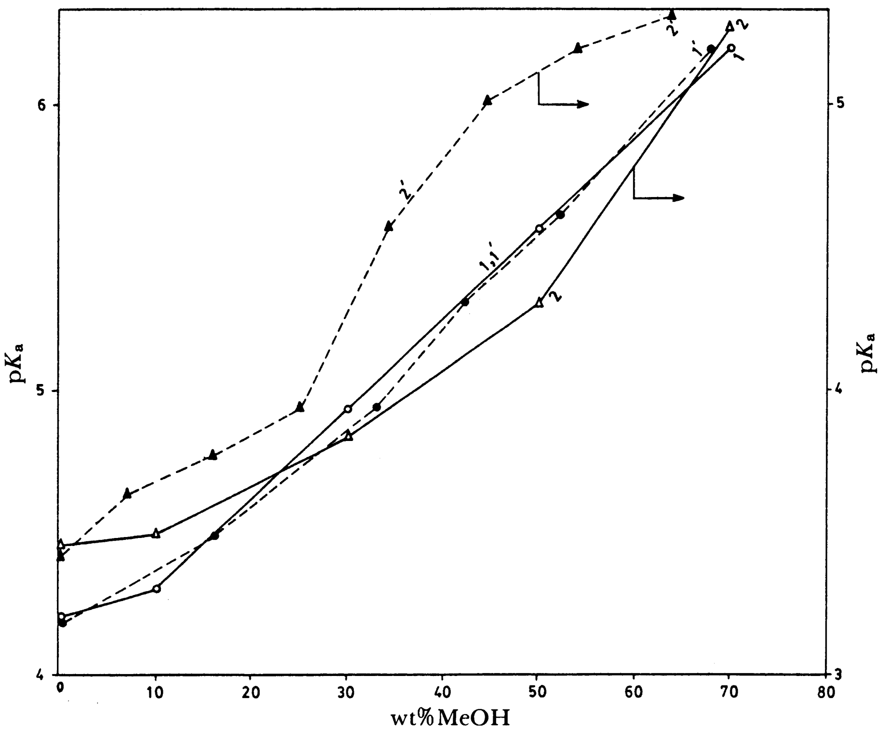

Fig. 1. Dependence of pK_a values of benzoic (○,●) and 4-nitrobenzoic acids (△,▲) on composition of MeOH-H_2O mixtures at 298 K: 1, 2 present work; 1′, 2′ taken from Refs. 26 and 19.

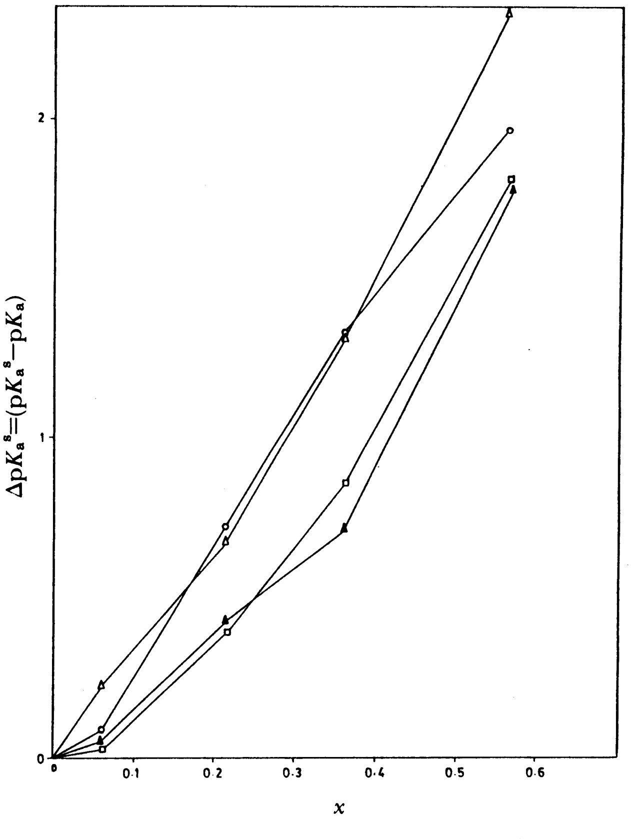

Fig. 2. Effect of changes of solvent composition on the pK_a values of benzoic (○); 2-nitrobenzoic (△); 3-nitrobenzoic (▲); and 4-nitrobenzoic (□) acids in $x\{CH_3OH+(1-x)\ H_2O\}$ at 298 K.

energy of transfer from aqueous to aqueous-methanol mixtures is playing a dominant role. It means that these are specific chemical interactions going on between ions of these acids and the solvent.

The dissociation order in respect of the acids studied in MeOH-H_2O mixtures turns out to be; 2-nitrobenzoic acid > 3-nitrobenzoic acid ≃ 4-nitrobenzoic acid > benzoic acid. This observed difference of acidities among the same isomers of nitrobenzoic acid could be explained on basis of intramolecular hydrogen bonding, inductive and resonance effects of the substituent and its respective position on the benzene ring with respect to carboxyl group.[25]

The normalized Walden products ($\Lambda_0\eta/\Lambda_{0w}\eta_w$) against percentage of methanol in MeOH-H_2O system, decreases as the solvent mixture is enriched in methanol. The changes in the Walden product are not only due to viscosity or dielectric constant variations but also to an altering proton transfer mechanism.[7]

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