Thermodynamic Dissociation Constants of Benzoic and Nitrobenzoic Acids in Binary Mixtures of Water with Acetone and Tetrahydrofuran at 25 °C

M. Sadiq Khan Niazi,* A. Hassan, M. Zafar I. Khan, S. S. Shah, and J. Ali

Department of Chemistry, Quaid-I-Azam University, Islamabad, Pakistan

The dissociation constants and limiting molar conductances of benzoic and 2-, 3-, and 4-nitrobenzoic acids have been determined in binary mixtures of water with acetone and tetrahydrofuran at 25 °C, respectively. The experimental data were analyzed by means of the Lee and Wheaton equation. The results are compared with those available in literature and in other water + cosolvent mixtures.

Introduction

The thermodynamic dissociation constants (pK_a) values of benzoic acid 2-, 3-, and 4-nitrobenzoic acids are available in a few water + acetone mixtures which were derived from conductometric data (*1*). The pK_a values for benzoic and 2- and 3-nitrobenzoic acids are also available in the literature in a few acetone + water mixtures mainly derived potentiometrically (*2*, *3*).

The present paper is on the study of the dissociation of these acids in binary mixtures of water with acetone and tetrahydrofuran, ranging in composition from 0 to 50% mass/mass of the cosolvent. The molar conductances of the dilute solutions of the acids have been measured at 25 °C. The conductance–concentration data have been analyzed for the derivation of pK_a and limiting molar conductance, Λ_o, values. The results are compared with those previously found by others in acetone + water, alcohol + water, and acetonitrile + water (*4*–*6*).

Experimental Section

The acids were the same as those used in previous studies (*4*–*6*). The solvents were from E. Merck and were purified further as detailed elsewhere (*7*).

Conductance measurements were carried out using an autobalance precision bridge (Wyne Kerr, B641) working at 1592 Hz in the same way as detailed earlier (*8*). Two different cells with cell constants 0.876 and 1.111 ± 0.002 cm^{-1} were used. The cells were calibrated with aqueous KCl solutions as recommended by Fuoss and co-workers (*9*). The reproducibility of the conductance measurement was better than ±0.5%. The conductance data are given in Tables II and III for each acid in different water + cosolvent. The accuracy of conductance data is better than ±0.2%. No solvent corrections were applied. The densities (ρ) and viscosities (η) of water + cosolvent were measured in the same way as detailed elsewhere (*10*). The values of dielectric constants for acetone + water and tetrahydrofuran + water were taken from the literature (*11*, *12*), and these physical properties are collected in Table I. Triply distilled water was used as an aqueous medium and for the preparation of solvent mixtures. The conductivity cell was placed in an oil bath thermostated at 25 ± 0.01 °C.

Results and Discussion

The experimental data were treated by the method proposed by Pethybridge and Taba, using the Lee and Wheaton equation in its series form (*13*, *14*). The molar conductances at infinite dilution, Λ_o, standard deviations, σ_Λ (%), based on the observed and calculated Λ values, and association constants, K_A, for the process

$$H^+ + A^- \underset{K_a}{\overset{K_A}{\rightleftharpoons}} H^+A^- \qquad \text{(a)}$$

are listed in Tables IV and V for the four acids for each solvent system and were deduced from the equations

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

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

$$-(\ln f) = \beta k/2(1 + kR) \qquad \beta = e^2/DkT \qquad (3)$$

for Λ_o and K_A values which minimize

$$\sigma_\Lambda = [\sum_j [\Lambda_j(\text{calcd}) - \Lambda_j(\text{obsd})]^2/(n - 2)]^{1/2} \qquad (4)$$

by a least-squares analysis, using a computer program supplied by Dr. Gilkerson. The symbols have their usual meanings and are described fully in a previous paper (*15*).

No minimum was observed in the R vs σ_Λ (%) plot (*16*). As R was varied the accompanying values of Λ_o and K_A that minimize σ_Λ (%) also changed. Increasing R shifts the calculated conductance curve upward while increasing association shifts it downward. Λ_o changes very little while the K_A value changes about 0.5–1% for a unit change in R depending on the value of K_A and on the dielectric constant of the solvent medium (*17*). In the final analysis, the distance of closest approach R was set equal to the Bjerrum distance (3–8 Å) for these acids.

Table I. Densities, ρ, Viscosities, η, and Dielectric Constants, ϵ, for Acetone + Water and Tetrahydrofuran + Water at 25 °C

mass %	ρ/ (g cm^{-3})	η/ (mPa s^{-1})	ϵ	mass %	ρ/ (g cm^{-3})	η/ (mPa s^{-1})	ϵ
			Acetone				
0	0.9971	0.890	78.54	40	0.9398	1.345	55.65
10	0.9832	1.092	73.20	50	0.9211	1.228	50.15
20	0.9717	1.272	67.60	60	0.9000	1.036	43.48
30	0.9580	1.358	62.00	70	0.8870	0.814	37.30
			Tetrahydrofuran				
10	0.9933	1.199	71.76	50	0.9572	1.718	39.96
20	0.9876	1.500	64.60	60	0.9467	1.529	32.00
30	0.9795	1.710	56.59	70	0.9326	1.259	24.62
40	0.9694	1.785	48.20				

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Table II. Molar Conductances, Λ, for Solutions of Acids in Acetone + Water at 25 °C and Varying Concentrations of Cosolvent

10^4C/(mol dm^{-3})	Λ/(S cm^2 mol^{-1}) 10 mass %	20 mass %	30 mass %	40 mass %	50 mass %
	2-Nitrobenzoic Acid				
1.923	299.94	242.34	153.07	84.04	49.80
3.703	282.91	220.54	132.50	68.33	39.01
5.355	270.09	205.66	120.07	60.41	33.68
6.896	259.83	194.62	111.48	55.06	30.43
8.333	251.64	186.03	105.10	51.26	28.02
9.677	244.63	179.09	100.13	48.30	26.28
10.937	238.71	173.35	96.12	46.09	24.94
12.121	233.69	168.50	92.81	44.24	23.92
13.235	229.27	164.35	90.01	42.68	22.95
14.285	225.37	160.74	87.61	41.38	22.19
15.277	221.91	157.57	85.53	40.26	21.54
16.216	218.75	154.76	83.70	39.08	20.98
17.105	215.99	152.25	82.09	38.42	20.48
17.948	213.45	150.00	80.64	37.66	20.04
18.750	211.13	147.95	79.33	37.00	19.66
	3-Nitrobenzoic Acid				
1.923	200.700	124.72	84.19	39.85	28.21
3.703	165.630	98.60	65.59	30.19	21.19
5.355	146.470	85.45	56.47	25.66	17.95
6.896	133.910	77.17	50.81	22.91	15.99
8.333	124.900	71.39	46.87	21.03	14.65
9.677	118.040	67.07	43.94	19.64	13.67
10.937	114.83	65.05	42.58	19.00	13.22
12.121	108.17	60.93	39.82	17.93	12.31
13.235	104.46	58.66	38.30	17.00	11.81
14.285	101.33	56.72	37.02	16.41	11.40
15.277	98.63	55.12	35.93	15.90	11.04
16.216	96.28	53.70	34.98	15.47	10.73
17.105	94.20	52.46	34.15	15.10	10.46
17.948	92.37	51.36	33.42	14.75	10.23
18.750	90.73	50.33	32.77	14.45	10.02
	Benzoic Acid				
1.191	139.62	81.24	44.92	29.74	14.49
2.273	108.71	61.96	33.75	22.15	11.42
3.261	93.70	52.92	28.64	18.72	9.61
4.167	84.46	47.44	25.58	16.68	8.54
5.000	78.07	43.69	23.50	15.30	7.82
5.769	73.34	40.94	21.98	14.30	7.29
6.482	69.67	38.81	20.80	13.52	6.89
7.143	66.73	37.12	19.87	12.90	6.37
7.759	64.32	35.72	19.11	12.40	6.21
8.333	62.29	34.56	18.48	11.98	6.10
8.871	60.56	33.57	17.93	11.63	5.91
9.375	59.07	32.72	17.47	11.33	5.75
9.849	57.77	31.97	17.06	11.06	5.62
10.294	56.62	31.32	16.71	10.82	5.50

10^4C/(mol dm^{-3})	Λ/(S cm^2 mol^{-1}) 10 mass %	20 mass %	10^4C/(mol dm^{-3})	Λ/(S cm^2 mol^{-1}) 30 mass %	40 mass %	50 mass %
	4-Nitrobenzoic Acid					
0.961	229.43	171.98	1.913	84.73	53.66	31.54
1.851	199.56	143.45	3.703	66.05	40.32	23.67
2.677	181.30	127.54	5.355	56.88	34.77	20.04
3.447	168.60	117.00	6.896	51.18	31.08	17.85
4.165	159.14	109.36	8.333	47.22	26.68	16.36
4.837	151.73	103.54	9.677	44.27	25.24	15.27
5.468	145.73	98.89	10.397	41.79	24.18	14.42
6.059	140.79	95.11	12.121	40.73	23.13	13.74
6.599	136.73	92.04	13.235	38.61	23.13	13.19
7.140	133.03	89.26	14.285	37.32	22.33	12.72
7.637	129.90	86.93	15.277	36.23	21.65	12.33
8.107	127.16	84.90	16.216	35.28	20.55	11.98
8.550	124.75	83.12	17.105	34.45	20.09	11.69
8.971	122.58	81.54	17.948	33.71	19.69	11.43
9.375	120.63	80.11	18.750	33.06	19.60	11.19

Conductance Results. Tables IV and V show that the Λ_0 values for 2-, 3-, and 4-nitrobenzoic and benzoic acids decrease with the addition of either acetone or tetrahydrofuran. This may be due to a relative increase in viscosity values of acetone + water and tetrahydrofuran + water

Table III. Molar Conductances, Λ, for Solutions of Acids in Tetrahydrofuran + Water at 25 °C and Varying Concentrations of Cosolvent

10^4C/(mol dm^{-3})	Λ/(S cm^2 mol^{-1}) 10 mass %	20 mass %	30 mass %	40 mass %	50 mass %
	2-Nitrobenzoic Acid				
1.923	267.26	190.25	113.37	60.84	32.52
3.703	253.97	170.99	94.67	47.49	25.09
5.355	243.74	158.24	84.20	40.93	21.51
6.896	235.54	149.00	77.26	36.84	19.30
8.333	228.78	141.87	72.24	33.99	17.78
9.677	223.08	136.14	68.41	31.88	16.65
10.937	218.20	131.48	65.35	30.23	15.78
12.121	213.92	127.56	62.85	28.90	15.06
13.235	210.22	124.20	60.77	27.80	14.48
14.285	206.90	121.31	58.95	26.88	13.98
15.277	203.18	118.76	57.45	26.09	13.58
16.216	201.30	116.52	56.11	25.40	13.21
17.105	198.90	114.52	54.94	24.81	12.89
17.948	196.72	112.73	53.90	24.28	12.61
18.750	194.71	147.95	52.95	23.80	12.36
	3-Nitrobenzoic Acid				
1.923	186.69	114.92	80.40	42.23	23.18
3.703	154.60	91.07	62.48	32.20	17.27
5.355	136.04	79.14	53.72	27.53	14.58
6.896	129.55	71.58	48.30	24.53	12.97
8.333	121.21	66.28	44.52	22.53	11.86
9.677	114.82	62.31	41.72	21.06	11.06
10.937	109.74	59.20	39.55	19.93	10.44
12.121	107.57	56.68	37.78	19.02	10.44
13.235	102.08	54.58	36.35	18.26	10.02
14.285	99.13	52.86	35.12	17.63	9.54
15.277	96.56	51.33	34.09	17.09	9.20
16.216	94.32	50.02	33.20	16.63	8.88
17.105	92.36	48.87	32.40	16.23	8.66
17.948	90.60	47.85	31.70	15.86	8.25
18.750	89.03	46.93	31.08	15.55	8.08
	Benzoic Acid				
1.191	102.50	50.02	23.72	13.33	6.67
2.273	78.45	37.37	17.52	9.77	4.87
3.261	67.10	31.63	14.75	8.20	4.08
4.167	60.21	28.20	13.12	7.28	3.62
5.006	55.49	25.88	12.01	6.66	3.30
5.769	52.01	24.19	11.21	6.21	3.08
6.482	49.33	22.89	10.60	5.86	2.91
7.143	47.18	21.86	10.11	5.59	2.77
7.759	45.43	21.01	9.71	5.37	2.66
8.333	43.96	20.30	9.38	5.18	2.56
8.871	42.70	19.71	9.10	5.03	2.49
9.375	41.62	19.19	8.86	4.89	2.40
9.849	40.68	18.74	8.65	4.77	2.36
10.294	39.86	18.35	8.46	4.67	2.31
10.714	38.46	17.99	8.30	4.58	2.26

10^4C/(mol dm^{-3})	Λ/(S cm^2 mol^{-1}) 10 mass %	10^4C/(mol dm^{-3})	Λ/(S cm^2 mol^{-1}) 20 mass %	30 mass %	40 mass %	50 mass %
	4-Nitrobenzoic Acid					
0.961	206.50	1.923	126.70	77.54	47.73	28.03
1.851	180.40	3.703	102.65	61.08	36.60	21.04
2.677	164.30	5.355	89.96	52.73	31.35	17.84
3.447	153.00	6.896	81.80	47.72	28.05	15.92
4.165	144.58	8.333	76.00	44.10	25.81	14.61
4.837	138.00	9.677	71.63	41.41	24.21	13.61
5.468	132.57	10.937	68.18	39.30	22.93	12.84
6.059	128.12	12.121	65.40	37.60	21.85	12.27
6.599	124.36	13.235	63.00	36.18	20.96	11.79
7.140	121.13	14.285	61.07	35.10	20.24	11.35
7.637	118.32	15.277	59.42	34.00	19.63	10.97
8.107	115.84	16.216	57.95	33.13	19.08	10.65
8.550	113.90	17.105	56.66	32.32	18.60	10.39
8.971	111.70	17.948	55.51	31.67	18.30	10.13
9.375	110.00	18.750	54.50	31.06	17.88	10.05

Table IV. Conductance Parameters for Acids in Acetone + Water at 25 °C

mass % of acetone	Λ_0/ (S cm^2 mol^{-1})	K_A/ (dm^3 mol^{-1})	pK_a (±0.01)	σ_A/ %
	2-Nitrobenzoic Acid			
10	325.09 ± 0.07	455 ± 0.4	2.658	0.007
20	280.35 ± 0.02	934 ± 1	2.970	0.011
30	200.88 ± 0.03	2121 ± 4	3.331	0.008
40	139.80 ± 0.36	5806 ± 18	3.764	0.023
50	110.56 ± 0.36	14288 ± 65	4.155	0.019
	3-Nitrobenzoic Acid			
10	316.27 ± 0.03	4766 ± 4	3.678	0.008
20	256.64 ± 0.19	11473 ± 42	4.059	0.019
30	197.54 ± 0.07	16676 ± 48	4.222	0.005
40	135.22 ± 0.15	42838 ± 67	4.632	0.004
50	112.74 ± 0.14	63180 ± 82	4.811	0.003
	4-Nitrobenzoic Acid			
10	296.30 ± 0.03	3926 ± 2	3.594	0.015
20	257.83 ± 0.01	7855 ± 4	3.895	0.004
30	198.83 ± 0.04	16703 ± 13	4.242	0.004
40	171.63 ± 0.07	37218 ± 45	4.570	0.005
50	130.06 ± 0.11	68153 ± 62	4.833	0.005
	Benzoic Acid			
10	334.81 ± 0.03	29787 ± 76	4.474	0.003
20	254.39 ± 0.10	59566 ± 85	4.775	0.010
30	188.12 ± 0.03	147265 ± 112	5.168	0.005
40	160.69 ± 0.01	256094 ± 132	5.408	0.002
50	127.72 ± 0.04	997699 ± 234	5.999	0.007

Table V. Conductance Parameters for Acids in Tetrahydrofuran + Water at 25 °C

mass % of THF	Λ_0/ (S cm^2 mol^{-1})	K_A/ (dm^3 mol^{-1})	pK_a (±0.01)	σ_A/ %
	2-Nitrobenzoic Acid			
10	286.26 ± 0.04	377 ± 0.3	2.576	0.032
20	226.48 ± 0.05	1170 ± 0.8	3.068	0.028
30	169.98 ± 0.11	3943 ± 7	3.595	0.012
40	140.98 ± 0.09	9214 ± 54	3.964	0.029
50	85.72 ± 0.02	22955 ± 111	4.360	0.012
	3-Nitrobenzoic Acid			
10	289.20 ± 0.10	4470 ± 4	3.650	0.024
20	228.36 ± 0.54	9880 ± 12	4.015	0.027
30	194.10 ± 0.14	18060 ± 32	4.256	0.011
40	131.38 ± 0.13	34828 ± 87	4.542	0.007
50	111.98 ± 0.34	98383 ± 123	4.993	0.020
	4-Nitrobenzoic Acid			
10	263.18 ± 0.05	3643 ± 2	3.560	0.036
20	220.80 ± 0.12	6820 ± 9	3.833	0.012
30	164.08 ± 0.34	12508 ± 45	4.097	0.023
40	134.20 ± 0.38	27035 ± 65	4.431	0.014
50	112.47 ± 0.18	64376 ± 88	4.808	0.027
	Benzoic Acid			
10	307.28 ± 0.04	35892 ± 54	4.555	0.005
20	243.74 ± 0.05	73282 ± 63	4.865	0.008
30	175.62 ± 0.04	169824 ± 112	5.230	0.010
40	152.27 ± 0.03	463447 ± 132	5.686	0.006
50	118.79 ± 0.03	1584893 ± 221	6.200	0.003

mixtures, respectively (see Table I). Similar results were found in alcohol + water and acetonitrile + water mixtures (*4–7*). This may be due to a difference of differentiating ion solvation by the solvent molecules.

There is only one conductometric study on these acids in 10% and 25% acetone + water (*1*). Our values in 10% and 20% acetone + water are almost in good agreement with these values. No such study has been found in other acetone + water or tetrahydrofuran + water mixtures so that a comparison could be made.

Dissociation Constant Values. The pK_a values listed in Tables IV and V are correct to ±0.01. These values increased with the increase in the contents of the cosolvent in these solvent mixtures. This may be attributed to a decrease in polarity and dielectric constant of acetone + water and tetrahydrofuran + water mixtures.

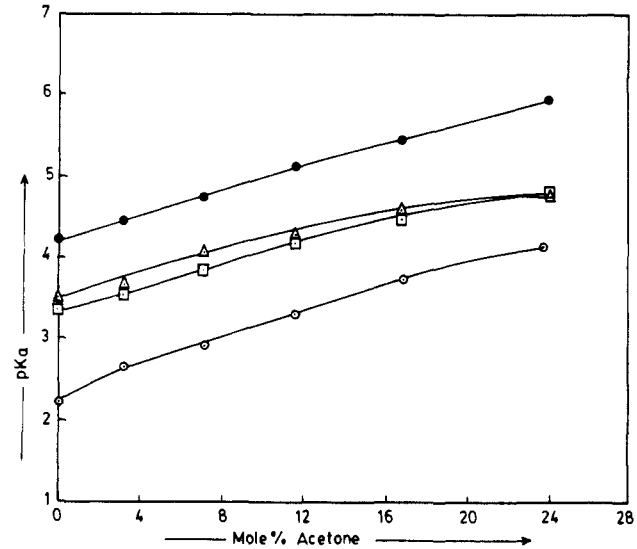

Figure 1. Dependence of thermodynamic dissociation constant values for 2-nitrobenzoic (○), 3-nitrobenzoic (△), 4-nitrobenzoic (□), and benzoic (●) acids on the composition of acetone + water mixtures at 25 °C.

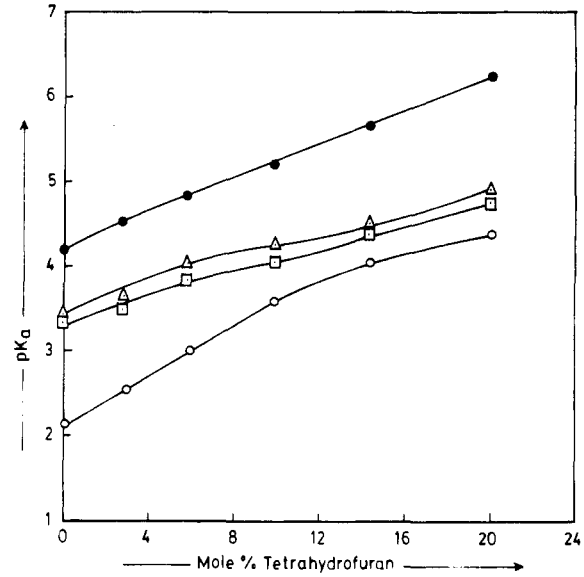

Figure 2. Dependence of thermodynamic dissociation constant values for 2-nitrobenzoic (○), 3-nitrobenzoic (△), 4-nitrobenzoic (□), and benzoic acids on the composition of tetrahydrofuran + water mixtures at 25 °C.

The dependence of pK_a values on the composition of water + cosolvent mixtures is shown in Figures 1 and 2. These figures show that the plots are nonlinear. Such nonlinear plots are also obtained if we plot pK_a values against the inverse of dielectric constant values, $1/\epsilon$, of water + cosolvent mixtures (not shown here). It means that, in addition to simple Born-type interactions (*18*), there are specific solute–solvent interactions. Further, each solvent system is acting differently toward each acid.

The pK_a values for benzoic and nitrobenzoic acids are available in some water + acetone mixtures (*1–3*). For tetrahydrofuran + water, only pK_a values for benzoic acid have been found (*2*). Presently found values are almost in agreement with the values derived by Dippy et al. (*1*) and differ with those found by Singh et al. It may be due to various approximations used in the determination of pH* values in mixed solvent systems.

Finally it has been found that the acids dissociate in these solvent systems as 2-nitrobenzoic acid > 4-nitrobenzoic acid ≥ 3-nitrobenzoic acid > benzoic acid.

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