Conductivities and Thermodynamic Dissociation Constants for Salicylic Acid in Binary Mixed Solvent Systems at 298.15 K

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The electrical conductivities for dilute solutions of salicylic acid in binary mixtures of *N,N*-dimethylformamide, acetone, tetrahydrofuran, methanol, ethanol, and 1-propanol with water have been measured at 298.15 K. The data were analyzed with the Lee–Wheaton conductance equation for the derivation of thermodynamic dissociation constants and limiting molar conductivities. The results were compared with those in the literature pertaining to analogous media, mostly derived potentiometrically.

Introduction

Salicylic acid and its alkali-metal salts have been of particular use as buffers for the pH* measurements both in aqueous medium as well as in mixed solvents (*1–4*). The pK_a (thermodynamic dissociation constant) values for salicylic acid are known in some alcohols + water, acetone + water, and *N,N*-dimethylformamide + water, mainly derived potentiometrically (*5–12*). The literature survey reveals that no conductivity measurements have been carried out on salicylic acid in these binary solvents and in those of tetrahydrofuran + water, except in methanol + water (*7*).

The conductometric method is the simple method for the determination of pK_a values of comparatively strong carboxylic acids. Further, it requires no buffers for the calibration of the electrode assembly. The molar conductivities of dilute solutions of salicylic acid in the binary mixtures of *N,N*-dimethylformamide, acetone, methanol, ethanol, and 1-propanol with water ranging in composition from 0 to 70 mass % of the cosolvent have been measured at 298.15 K. The thermodynamic dissociation constants, pK_a, and limiting molar conductivities, Λ_0, were derived from the conductance–concentration data. The results are compared with those reported by other researchers from potentiometric measurements.

Experimental Section

The salicylic acid (from BDH, extra pure) was recrystallized from an ethanol + water mixture, dried under vacuum over P_2O_5, and stored in a desiccator. The melting point of the dacid was 160–162 °C.

The solvents were the same as those used in previous studies, and their purification has been detailed in these papers (*13–15*). The fractionally distilled solvents had specific conductivities less than (1–3) × 10^{-7} S·cm^{-1}. Triply distilled water with the specific conductivity less than 10^{-6} cm^{-1}·Ω^{-1} was used for the preparation of binary mixtures and as an aqueous medium. The conductivity measurements were carried out using an automatic Microprocessor Model LF 2000 conductivity meter (Germany) which works at 1 kHz. The conductance cell was the same as detailed earlier (*13–15*). Two platinized platinum electrodes with cell constants of 0.998 ± 0.001 and 0.685 ± 0.001 cm^{-1} were used. Dry nitrogen was used to prevent the admission of air into the cell when solvent or stock solution was added. The cell was calibrated following the method of Wu and co-workers (*16*), using aqueous KCl solution. The concentrations (M) for the acid were kept constant for each solvent mixture, and no buoyancy corrections were made while calculating the molar conductance of acid solutions. The measurements were made at a temperature of 25 ± 0.01 °C.

Table I. Molar Conductivities, Λ, for Salicylic Acid in Water + Cosolvent Mixtures at 298.15 K[a]

10^4/ (mol·dm^{-3})	Λ/(S·cm^2·mol^{-1})						10^4c/ (mol·dm^{-3})	Λ/(S·cm^2·mol^{-1})	
	x_1 = 0	x_1 = 10	x_1 = 20	x_1 = 30	x_1 = 40	x_1 = 50		x_1 = 60	x_1 = 70
N,N-Dimethylformamide (1) + Water (2)									
1.923	341.04	252.33	185.80	138.26	97.42	71.05	1.191	43.23	36.05
3.703	313.49	229.56	167.76	123.33	85.40	60.93	2.773	34.58	27.77
5.355	294.15	214.03	155.73	113.66	77.94	54.94	3.261	30.19	25.00
6.896	279.57	202.50	146.90	106.68	72.68	50.84	4.167	27.42	22.13
8.333	268.07	193.54	140.06	101.36	68.73	47.83	5.000	25.49	21.06
9.677	258.71	186.30	134.62	97.14	65.63	45.49	5.769	24.04	17.50
10.937	250.92	180.31	130.08	93.68	63.11	43.60	6.487	22.91	16.66
12.121	244.30	175.24	126.28	90.79	61.02	42.05	7.143	22.00	15.98
13.235	238.58	170.90	123.04	88.33	59.26	40.76	7.759	21.25	15.42
14.285	233.61	167.15	120.26	86.21	57.75	39.64	8.333	20.62	14.96
15.277	229.23	163.84	117.78	84.35	56.43	38.68	8.871	20.08	14.56
16.216	225.34	160.90	115.65	82.71	55.27	37.83	9.375	19.61	14.21
17.105	221.86	158.28	113.65	81.26	54.24	37.08	9.849	19.20	13.91
17.948	218.73	155.92	111.96	79.97	53.31	36.41	10.294	18.84	13.64
18.750	215.88	153.79	110.33	78.77	52.48	35.81	10.714	18.52	13.40
Acetone (1) + Water (2)									
1.923		257.17	187.34	129.89	89.07	53.77	1.191	37.46	18.28
3.703		232.34	162.61	109.86	72.65	42.86	2.773	27.39	14.23
5.355		215.71	147.43	98.35	63.90	37.29	3.261	25.68	12.27
6.896		203.41	136.97	90.60	58.22	33.77	4.167	23.23	11.06
8.333		194.05	129.19	84.97	54.18	31.29	5.000	21.54	10.22
9.677		186.48	123.11	80.62	51.12	29.41	5.769	20.26	9.61
10.937		180.25	118.21	77.13	48.71	27.95	6.487	19.30	9.13
12.121		175.00	114.15	74.28	46.75	26.70	7.143	18.52	8.74
13.235		170.52	110.73	71.90	45.03	25.80	7.759	17.87	8.43
14.285		166.63	107.81	69.86	43.73	24.97	8.333	17.33	8.16
15.277		163.33	105.26	68.09	42.55	24.26	8.871	16.86	7.94
16.216		160.22	103.01	66.55	41.50	23.75	9.375	16.46	7.74
17.105		157.53	101.03	65.19	40.59	23.11	9.849	16.11	7.57
17.948		155.11	99.27	63.97	39.78	22.62	10.294	15.80	7.42
18.750		152.93	97.66	39.05	39.05	22.19	10.714	15.70	7.29
Tetrahydrofuran (1) + Water (2)									
1.923		283.67	212.21	129.18	73.78	43.13			
3.703		250.07	179.02	105.10	58.96	33.38			
5.355		228.89	160.06	92.32	51.36	28.67			
6.896		213.98	147.30	84.06	46.61	25.75			
8.333		202.56	138.03	78.19	43.16	23.73			
9.677		193.64	130.92	73.75	40.57	22.22			
10.937		186.39	125.24	70.24	38.55	21.07			
12.121		180.33	120.57	67.39	36.91	20.12			
13.235		175.23	116.68	65.11	35.55	19.34			
14.285		170.82	113.31	63.02	34.40	18.69			
15.277		166.98	110.47	61.28	33.42	18.14			
16.216		163.61	107.95	59.78	32.57	17.67			
17.105		160.60	105.74	58.46	31.82	17.24			
17.948		157.93	103.77	57.30	31.16	16.87			
18.750		155.50	102.00	56.25	30.57	16.54			

[a] x_1 is in mass percent.

The densities (ρ), viscosities (η), and dielectric constants (ϵ) for solvent mixtures were taken from previous papers (*13–*

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Table II. Molar Conductivities, Λ, for Salicylic Acid in Water + Cosovent at 25 °C[a]

10^4c/ (mol·dm^{-3})	Λ/(S·cm^2·mol^{-1})					10^4c/ (mol·dm^{-3})	Λ/(S·cm^2·mol^{-1})	
	x = 10	x_1 = 20	x_1 = 30	x_1 = 40	x_1 = 50		x_1 = 60	x_1 = 70
Methanol (1) + Water (2)								
1.923	251.84	197.45	150.23	117.95	86.89	1.191	74.24	49.91
3.703	223.28	171.71	127.35	98.20	70.82	2.273	60.15	39.51
5.355	205.02	155.98	114.13	87.20	62.27	3.261	52.83	34.34
6.896	191.99	145.04	105.23	79.97	56.74	4.167	48.16	31.11
8.333	182.13	136.87	98.72	74.75	52.79	5.006	44.88	28.87
9.677	174.33	130.50	93.69	70.73	49.80	5.569	42.41	27.20
10.397	167.97	125.36	89.68	67.55	47.44	6.482	40.47	25.89
12.121	162.67	121.09	86.39	64.95	45.53	7.143	38.90	24.85
13.235	158.16	117.48	83.61	62.78	43.93	7.759	37.61	23.99
14.285	154.29	114.39	81.26	60.93	42.56	8.333	36.52	23.27
15.277	150.19	111.70	79.21	59.35	41.42	8.871	35.58	22.64
16.216	147.93	109.34	77.43	57.95	40.41	9.375	34.77	22.11
17.105	145.28	107.26	75.86	56.73	39.52	9.849	34.06	21.65
17.948	142.91	105.39	74.46	55.64	38.72	10.294	33.43	21.23
18.750	140.75	103.71	73.20	54.61	38.02	10.714	32.87	20.96
Ethanol (1) + Water (2)								
1.923	259.32	197.71	136.65	92.46	60.92	1.191	49.46	36.10
3.703	230.38	172.92	114.17	75.69	48.85	2.273	39.53	28.23
5.355	211.78	157.57	101.52	66.67	42.62	3.261	34.51	24.40
6.896	198.47	146.82	93.15	60.82	38.64	4.167	31.34	22.04
8.333	188.37	138.77	87.11	56.64	35.85	5.000	29.13	20.40
9.677	180.35	132.44	82.49	53.46	33.74	5.769	27.48	19.19
10.937	178.82	127.32	78.81	50.95	32.08	6.482	26.19	18.25
12.121	168.36	123.08	75.81	48.91	30.73	7.143	25.15	17.49
13.235	163.72	119.48	73.30	47.21	29.62	7.759	24.29	16.87
14.285	159.74	116.40	71.16	45.77	28.68	8.333	23.57	16.35
15.277	156.22	113.73	69.32	44.52	27.88	8.871	22.95	16.35
16.216	153.24	111.36	67.72	43.47	27.18	9.375	15.19	15.91
17.105	150.39	109.27	66.30	42.52	26.55	9.849	15.53	15.53
17.948	147.94	107.41	65.05	41.68	26.02	10.294	15.19	12.89
18.750	145.73	105.72	63.90	40.94	25.53	10.714	14.89	12.64
1-Propanol (1) + Water (2)								
1.923	254.27	165.96	104.85	70.84	44.24	1.191	31.14	18.64
3.703	224.92	138.18	84.79	56.82	34.69	2.273	24.19	14.24
5.355	206.25	122.74	74.26	49.42	29.90	3.261	20.84	12.19
6.896	192.96	112.52	67.50	44.88	26.93	4.167	18.79	10.94
8.333	182.91	105.14	62.72	41.62	24.86	5.000	17.38	10.09
9.677	174.97	99.47	59.10	39.17	23.31	5.769	16.33	9.46
10.937	168.51	95.03	56.25	37.25	22.12	6.482	15.52	8.98
12.121	163.12	91.37	53.94	35.69	21.15	7.143	14.87	8.59
13.235	158.55	88.31	52.02	34.41	20.36	7.759	14.34	8.27
14.285	154.60	85.71	50.39	33.22	19.69	8.333	13.89	8.01
15.277	151.17	83.42	49.00	32.39	19.11	8.871	13.51	7.78
16.216	148.15	81.53	47.79	31.58	18.62	9.375	13.18	7.59
17.105	145.46	79.80	46.72	30.87	18.18	9.849	12.89	7.42
17.948	143.05	78.27	45.77	30.27	17.80	10.294	12.64	7.27
18.750	140.88	76.90	44.92	29.67	17.46	10.714	12.41	7.14

[a] x_1 is in mass percent.

15). The other procedures were the same as those detailed earlier (*13–15*).

Results and Discussion

The molar conductivities for solutions of salicylic acid in different solvent systems are given in Tables I and II, respectively. The experimental data were analyzed with the Lee and Wheaton conductance equation in series form as suggested by Pethybridge and Taba (*17, 18*). The limiting molar conductivity, Λ_0, and association constants $K_A = 1/K_a$ for the process

$$\mathrm{H^+ + A^- \underset{K_a}{\overset{K_A}{\rightleftharpoons}} H^+A^-} \tag{1}$$

were deduced from the set of equations

$$\Lambda = \alpha[\Lambda_0(1 + \Delta X/X) - \Delta\Lambda_{el}] \tag{2}$$

Table III. Conductance Parameters for Salicylic Acid in Water + Cosolvent Mixtures at 298.15 K

x_1/ (mass %)	Λ_0/ (S·cm^2·mol^{-1})	$10^{-3}K_A$/ (dm^3·mol^{-1})	$100\sigma_\Lambda/\Lambda_0$	10^8q/cm
N,N-Dimethylformamide (1) + Water (2)				
0	384.23 ± 0.23	0.884 ± 0.004	0.010	3.568
10	292.03 ± 0.01	1.004 ± 0.006	0.010	3.650
20	218.41 ± 0.04	1.188 ± 0.013	0.023	3.754
30	167.19 ± 0.01	1.409 ± 0.021	0.014	3.892
40	123.23 ± 0.01	1.843 ± 0.028	0.021	4.066
50	96.09 ± 0.01	3.488 ± 0.036	0.013	4.314
60	60.68 ± 0.03	6.310 ± 0.044	0.018	4.634
70	43.21 ± 0.12	19.179 ± 0.058	0.023	5.049
Acetone (1) + Water (2)				
10	302.13 ± 0.06	1.259 ± 0.006	0.035	3.828
20	244.38 ± 0.02	2.612 ± 0.011	0.020	4.145
30	184.62 ± 0.02	3.972 ± 0.019	0.012	4.599
40	149.28 ± 0.13	7.691 ± 0.030	0.022	5.036
50	103.78 ± 0.11	14.997 ± 0.054	0.032	5.588
60	67.04 ± 0.05	21.888 ± 0.074	0.030	6.444
70	44.79 ± 0.04	38.748 ± 0.088	0.033	7.512
Tetrahydrofuran (1) + Water (2)				
10	353.38 ± 0.06	1.621 ± 0.011	0.028	3.905
20	304.55 ± 0.05	3.488 ± 0.015	0.016	4.338
30	219.62 ± 0.04	6.211 ± 0.032	0.025	4.957
40	141.12 ± 0.11	9.287 ± 0.044	0.027	5.811
50	109.34 ± 0.10	18.884 ± 0.064	0.030	7.006

Table IV. Conductance Parameters for Salicylic Acid in Water + Cosolvent Mixtures at 298.15 K

x_1/ (mass %)	Λ_0/ (S·cm^2·mol^{-1})	$10^{-3}K_A$/ (dm^3·mol^{-1})	σ_Λ	10^8q/cm
Methanol (1) + Water (2)				
10	308.92 ± 0.13	1.444 ± 0.001	0.020	3.776
20	255.43 ± 0.02	1.990 ± 0.001	0.022	4.002
30	211.64 ± 0.002	3.020 ± 0.002	0.017	4.383
40	178.64 ± 0.02	4.101 ± 0.004	0.026	4.599
50	146.16 ± 0.004	6.049 ± 0.007	0.044	5.079
60	130.96 ± 0.10	11.469 ± 0.010	0.016	5.419
70	103.57 ± 0.23	18.902 ± 0.011	0.028	6.000
Ethanol (1) + Water (2)				
10	316.61 ± 0.12	1.403 ± 0.002	0.029	3.849
20	251.83 ± 0.02	1.823 ± 0.003	0.026	4.183
30	204.18 ± 0.009	3.893 ± 0.004	0.100	4.512
40	152.21 ± 0.11	5.600 ± 0.005	0.125	5.093
50	113.41 ± 0.04	8.510 ± 0.010	0.044	5.777
60	95.70 ± 0.13	15.503 ± 0.011	0.135	6.456
70	84.67 ± 0.14	27.191 ± 0.012	0.171	7.635
1-Propanol (1) + Water (2)				
10	314.02 ± 0.01	1.511 ± 0.001	0.014	3.924
20	251.34 ± 0.08	4.106 ± 0.003	0.111	4.318
30	184.63 ± 0.03	7.092 ± 0.005	0.035	4.852
40	131.22 ± 0.11	8.588 ± 0.007	0.121	5.638
50	100.05 ± 0.19	15.100 ± 0.011	0.200	6.516
60	78.14 ± 0.14	32.643 ± 0.012	0.171	7.656
70	58.21 ± 0.20	57.368 ± 0.013	0.306	9.127

$$K_A = (1 - \alpha)/\alpha^2\gamma^2c \tag{3}$$

$$-\ln \gamma = bk/2(1 + kR), \quad b = e^2/DkT \tag{4}$$

which minimize the standard deviation

$$\sigma_\Lambda{}^2 = \sum_j [\Lambda_j(\text{calcd}) - \Lambda_j(\text{obsd})]^2/(n - 2) \tag{5}$$

where n is the number of data points. All the symbols have been described in previous papers (*13–15*).

In the case of carboxylic acids no minimum is observed in a R–σ_Λ (%) plot (*19*). The R (ion-pair distance) values were varied from 3 to 10 Å. The values of R used for salicylic acid were from 4 to 8 Å in different solvent mixtures. These values are actually equal to the Bjerrum distance (q) (*20*), as selected by some other researchers (*22*) according to the suggestion of Justice et al. (*21*). The conductance parameters of the

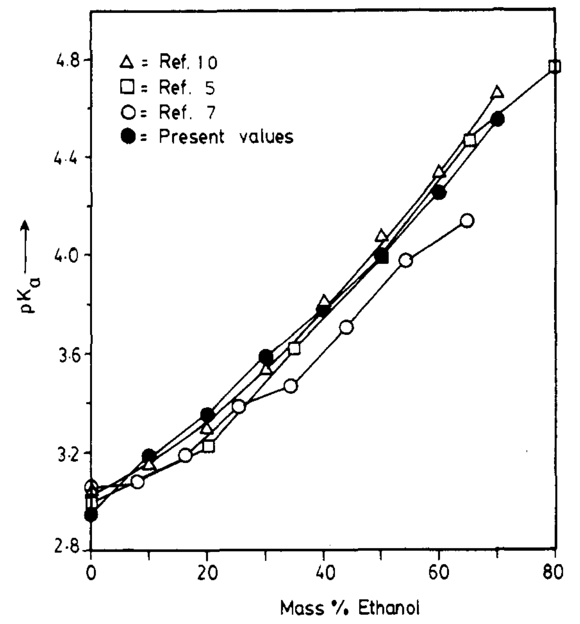

Figure 1. Comparison of pK_a values for salicylic acid showing dependence on the composition of ethanol + water mixtures at 298.15 K.

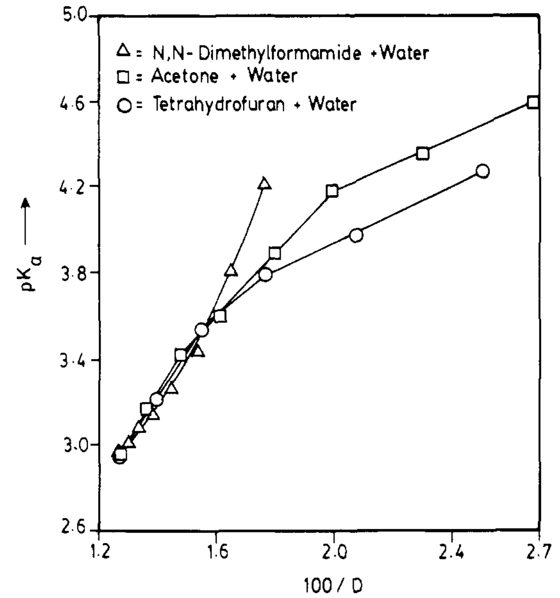

Figure 2. Dependence of thermodynamic dissociation constant values pK_a for salicylic acid on the inverse of the dielectric constants (100/D) of water + cosolvent at 298.15 K.

acid along with the Bjerrum distance parameter are collected in Tables III and IV.

(**a**) ***Limiting Molar Conductances.*** The Λ_0 value for salicylic acid aqueous solution was found to be 384.23 ± 0.23 S·cm^2·mol^{-1}. The literature values are 382.00, 385.2, and 400 S·cm^2·mol^{-1} (*6, 7, 11*). Tables III and IV show that the limiting molar conductances for the acid decreased with the increase in the contents of the cosolvent in the water. Similar results were found for nitrobenzoic and benzoic acids in these solvent mixtures (*13–15*). Dippy et al. (*12*) have reported Λ_0 values for salicylic acid in 10 and 25 mass % acetone + water as 315.4 and 238.3 S·cm^2·mol^{-1}, respectively, which are in close agreement with our values (Table III). Since Mandal et al. (*7*) have used different ethanol + water mixtures, no comparison could be made between the two sets of Λ_0 values.

(**b**) ***Thermodynamic Dissociation Constants.*** The pK_a value found for salicylic acid is 2.94 ● 0.01. This value is in complete agreement with those reported by others (*5–12*), which are 3, 2.98, and 3.01, derived either potentiometrically or conductometrically. Petrov et al. (*9*) have reported pK_a values for salicylic acid in some *N,N*-dimethylformamide + water mixtures of composition 0 and 70% v/v *N,N*-dimethylformamide. These values are 2.96 and 5.65. Singh et al. (*8*) have reported pK_a values for salicylic acid in 20, 30, 40, and 50 mass % acetone + water mixtures as 3.472, 3.681, 3.936, and 4.247, which were derived potentiometrically. Our values are 3.417, 3.599, 3.886, and 4.176 in the same solvent mixtures. The pK_a values for salicylic acid in ethanol + water mixtures derived presently and reported by others are compared in Figure 1.

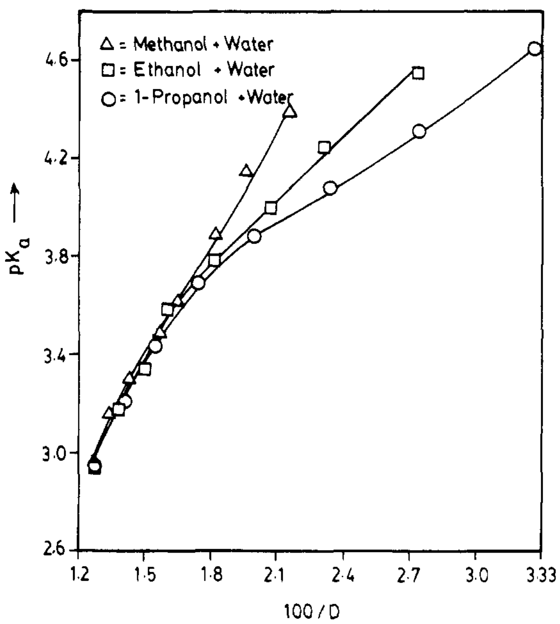

Figure 3. Dependence of thermodynamic dissociation constant values pK_a for salicylic acid on the inverse of dielectric constants (100/D) of water + cosolvent at 298.15 K.

Tables III and IV show that the pK_a values increased with the addition of cosolvent in water. The dependence of pK_a values for salicylic acid on the inverse of the permitivity (100/D) of water + cosolvent mixtures is shown in Figures 2 and 3. The figures indicate that, for the isodielectric solvent mixtures, different pK_a values have been found.

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