

Conductometric Study of Chloroacetic Acid in Binary Mixture of Water with N,N-dimethylformamide, Acetone and Acetonitrile at 298.15 K

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Summary: Molar conductances of dilute solutions of chloroacetic acid in binary mixtures of N,N-dimethylformamide, acetone and acetonitrile with water have been measured at 298.15 K. The data were fitted to the Lee - Wheaton conductance equation for the derivation of thermodynamic dissociation constants and limiting molar conductances. The results are discussed in terms of solvent effect on the ionization of acid as the composition of solvent mixture is varied.

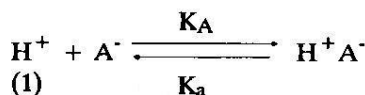
Introduction

Moderately strong carboxylic acids like salicylic and chloroacetic acids and their alkali metal salts have been of particular use as buffers for the calibration of pH meter both in aqueous as well as in mixed solvent systems [1-3]. Though the pK_a (thermodynamic dissociation constants) values of chloroacetic acid are known in aqueous, alcohol + water and a few N,N-dimethylformamide + water mixture [4-7], the literature survey shows that no such values are available for this acid in solvent mixtures of water with N,N-dimethylformamide, acetone and acetonitrile, respectively. 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 electrode assembly. Present paper reports the molar conductances of dilute solutions of chloroacetic acid in the binary mixtures of N,N-dimethylformamide, acetone and acetonitrile with water ranging in composition from 0-70 mass % of the cosolvent, at 298.15 K respectively. The thermodynamic dissociation constants pK_a and limiting molar conductances Λ_0 for the acid have been derived from the conductance - concentration data and are compared among these systems. The results are discussed in terms of solvent effect on the conductance parameters for the acid as the composition of solvent mixtures was varied.

Results and Discussion

The values of the molar conductances for solutions of different concentrations of the acid in

different solvent mixtures are given in Table 2. The experimental data were analyzed with the Lee and Wheaton conductance equation in series form as suggested by Pethybridge and Taba [11-12]. The limiting molar conductance Λ_0 and association constants $K_A = 1/K_a$ for the process:



were deduced from the set of equations

$$\Lambda_0 = \gamma [\Lambda_0 (1 + \Delta X/X) - \Delta \Lambda_{el}] \quad (2)$$

$$K_A = (1 - \gamma)/\gamma^2 f^2 c \quad (3)$$

$$-\ln f = Kb/2 (1 + KR); b = c^2/\sum KT \quad (4)$$

which minimize the standard deviation

$$\sigma^2 \Lambda = \sum (\Lambda_j(\text{cal}) - \Lambda_j(\text{obs}))^2 / (n - 2) \quad (5)$$

where n is the number of data points. All the symbols have been described in previous papers [8-9].

In the case of carboxylic acids no minimum is observed in a $R - \sigma$ (%) plot [13]. The R (ion-pair

Table 1: Densities, ρ , viscosities, η , and dielectric constant values ϵ for water + cosolvent mixtures at 25°C.

Cosolvent Mass %	$\rho/$ (g.cm ⁻³)	$\eta/$ (m Pa s)	ϵ
N,N-dimethylformamide + Water			
0	0.9971	0.890	78.54
10	0.9964	1.153	76.78
20	0.9963	1.326	74.65
30	0.9971	1.665	72.00
40	0.9968	2.042	68.92
50	0.9961	2.338	64.96
60	0.9934	2.491	60.48
70	0.9913	2.580	55.50
Acetone + Water			
10	0.9832	1.092	73.20
20	0.9717	1.272	67.60
30	0.9580	1.358	62.00
40	0.9398	1.345	55.65
50	0.9211	1.228	50.15
60	0.9000	1.036	43.48
70	0.8870	0.814	37.30
Acetonitrile + Water			
10	0.9800	0.980	74.66
20	0.9586	0.971	70.50
30	0.9388	0.912	65.78
40	0.9135	0.8843	60.20
50	0.8922	0.752	55.68
60	0.8666	0.657	50.77
70	0.8445	0.573	46.52

distance) values were varied from 3 to 10 Å. The values of R used for these acids were from 4 to 8 Å in different solvent mixtures. These values are actually = Bjerrum distance (q) [14] as selected by some other workers according to suggestion of Justice *et al.*, [15]. The conductance parameters of the acid in different solvent mixtures are collected in Table 3.

a) Limiting molar conductances.

The Λ_0 values for chloroacetic acid in aqueous solution is found to be 382.00 ± 0.05 S.cm².mol⁻¹. The literature values are 382, and 391.S.cm².mol⁻¹, respectively [4-5]. Table 3 shows that the limiting molar conductances for the acid decreased with the increase in contents of the cosolvent in the water. This decrease in the Λ_0 values may be attributed to relative increase in the viscosity values of water-cosolvent mixtures. Similar results were found for benzoic, nitrobenzoic acid salicylic acids in these solvent mixtures [8-9,16]. It may be also due to solvation of the ions by the solvent molecules.

Thermodynamic dissociation constants

The pK_a value found for chloroacetic acid is 2.859 ± 0.003 . This value is in complete agreement

Table 2: Molar conductances, Λ , for monochloroacetic acid in water + cosolvent mixture at 25°C.

	Mass % cosolvent								
	0	10	20	30	40	50	60	70	
10 ⁴ C/ (mol.m ⁻³)									
				$\Lambda/(S.cm.^2.mol^{-1})$					
10 ⁴ C (mol.dm ⁻³)									$\Lambda/(S.cm.^2.mol^{-1})$
N,N-dimethylformamide + Water									
1.923	308.68	258.04	188.31	131.69	79.79	52.48	1.191	45.25	31.85
3.703	285.45	233.63	168.89	117.35	70.37	44.62	2.273	38.61	26.32
5.355	268.90	217.18	156.12	108.09	64.34	40.05	3.261	34.77	23.33
6.896	256.28	205.06	146.84	101.42	60.04	36.95	4.167	32.19	21.35
8.333	246.28	195.69	140.72	96.33	56.88	34.68	5.006	30.32	20.01
9.677	238.03	188.15	134.04	92.35	54.35	32.93	5.769	28.13	18.96
10.937	231.18	181.93	129.39	88.99	52.30	31.53	6.482	27.72	18.13
12.121	225.31	176.70	125.49	86.32	50.60	30.38	7.143	26.78	17.46
13.235	220.26	172.22	122.16	83.88	49.15	29.41	7.759	25.99	16.90
14.285	215.85	168.33	119.29	81.86	47.92	28.59	8.333	25.31	16.43
15.277	211.94	164.94	116.78	80.09	46.83	27.88	8.871	24.73	16.02
16.216	208.46	161.90	114.56	78.35	45.88	27.26	9.375	24.23	15.67
17.105	205.35	159.21	112.58	77.14	45.03	26.71	9.849	23.78	15.36
17.948	202.53	156.79	110.80	75.90	44.28	26.21	10.294	23.29	15.09
18.750	199.99	154.60	109.20	74.78	43.60	25.77	10.714	23.04	14.84

Table 2: Continued

	Mass % cosolvent							
	0	10	20	30	40	50	60	70
$10^4 C/$					$10^4 C$			
(mol.m ⁻³)	$\Lambda/(S.cm.^2 mol^{-1})$				$(mol.dm^{-3}) \Lambda/(S.cm.^2 mo^{-1})$			
Acetone + Water								
1.923	268.50	195.30	141.06	87.92	51.06	1.191	37.70	24.76
3.703	241.49	168.96	116.97	70.44	40.03	2.273	29.58	19.11
5.355	223.59	153.03	103.71	61.44	34.57	3.261	25.60	16.41
6.896	210.53	142.04	94.98	55.71	31.15	4.167	23.14	16.07
8.333	200.50	133.90	88.70	51.68	28.79	5.006	21.43	13.63
9.677	192.48	127.56	83.92	48.64	26.96	5.769	20.16	12.80
18.937	185.89	122.45	80.12	46.26	25.61	6.482	19.17	12.15
12.121	180.36	118.23	77.02	44.33	24.49	7.143	18.38	11.63
13.235	175.63	114.67	74.43	42.73	23.58	7.759	17.73	11.21
14.285	171.55	111.62	72.23	41.38	22.80	8.333	17.18	10.85
15.277	167.97	108.98	70.34	40.22	22.13	8.871	16.72	10.55
16.216	164.81	106.66	68.69	39.22	21.56	9.375	16.32	10.29
17.105	161.98	104.60	67.24	38.34	21.05	9.849	15.96	10.06
17.948	159.47	102.77	65.95	37.55	20.61	10.294	15.65	9.86
18.750	157.15	101.13	64.79	36.85	20.21	10.714	15.38	9.68
Acetonitrile + Water								
1.923	269.16	209.00	150.34	102.71	63.59	1.191	46.35	30.63
3.703	244.24	182.86	125.84	89.91	50.09	2.273	36.78	23.87
5.355	227.27	166.70	112.10	72.56	43.34	3.261	31.98	20.59
6.896	214.79	155.35	102.97	65.89	39.11	4.167	28.98	18.56
8.333	205.08	146.85	96.32	61.19	36.16	5.006	26.88	17.17
9.677	197.29	140.18	91.22	57.64	33.94	5.769	25.32	16.13
10.937	190.86	134.78	87.18	54.85	32.20	6.482	24.11	15.33
12.211	185.44	130.28	83.86	52.58	30.82	7.143	23.13	14.68
13.235	180.80	126.48	81.09	50.70	29.65	7.759	22.32	14.15
14.285	176.76	123.22	78.74	49.11	28.69	8.333	21.67	13.71
15.277	173.25	120.38	76.73	47.74	27.86	8.871	21.07	13.33
16.216	170.12	117.89	74.92	46.55	27.14	9.375	20.57	13.00
17.105	167.24	115.68	73.36	45.50	26.51	9.849	20.19	12.72
17.948	164.73	113.70	71.97	44.58	25.94	10.294	19.74	12.47
18.750	162.43	111.92	43.75	43.75	25.44	10.714	19.40	12.24

with those reported in literature i.e. 2.86 and 2.91 [5-7], either derived potentiometrically or conductometrically. Only one study on the ionization of chloroacetic acid is available in a few N,N-dimethylformamide + water mixtures [7]. The pK_a values derived by them (potentiometrically) are 2.86 and 4.00 in 0 and 50 v/v of N,N-dimethylformamide. We were not able to find pK_a values for chloroacetic acid in other solvent mixtures so that a comparison could be made.

Table 3 shows that the pK_a values increased with the addition of cosolvent in water. This increase may be attributed to decrease in the values of dielectric constant of water-cosolvent mixtures. The pK_a values found for chloroacetic acid for N,N-dimethylformamide mixtures are lower

than those found for either acetone + water or acetonitrile + water mixtures. This may be due to higher dielectric constant values of former mixtures than those of later mixtures. Similarly pK_a values for acetonitrile + water are lower than those in acetone + water.

The dependence of pK_a values on the inverse of permittivity ($1/\epsilon$) of water-cosolvent mixtures is shown in Fig. 1. The figure indicate that for the isodielectric solvent mixtures, no same pK_a values for this acid have been found. It means that dielectric constant is not the sole parameter for the solvent which determines the extent of the dissociation of electrolyte in the solution. Further Fig. 2 shows that the plot of (ΔpK_a) (which is equal to $(pK_a^s - pK_a^w)$, where s refer to solvent mixture and

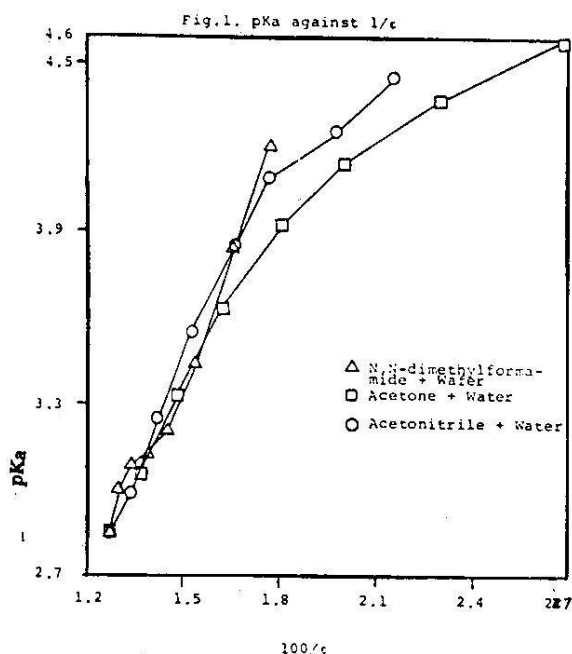


Fig. 1: Dependence of pK_a values for chloroacetic acid on the inverse of dielectric constant values ($1/\epsilon$) of water + cosolvent mixtures at 298.15 K.

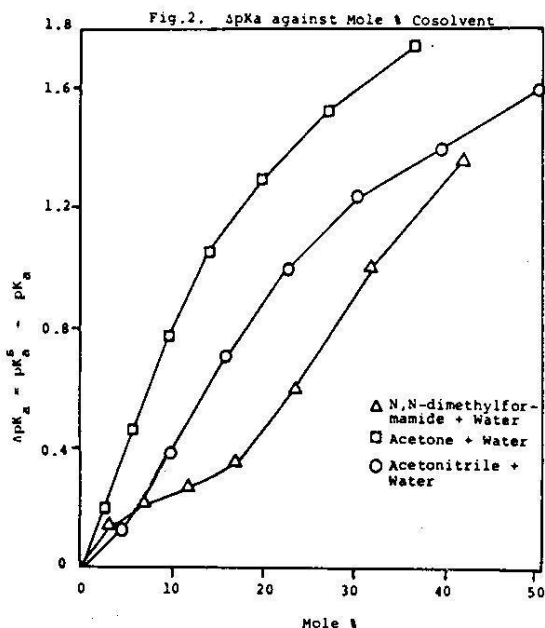


Fig. 2: Dependence of $\Delta pK_a = pK_a^S - pK_a^W$ for chloroacetic acid on the composition of water + cosolvent mixtures at 298.15 K.

Table 3: Conductance parameters for chloroacetic acid in water-cosolvent mixture at 25°C.

Mass %	Λ_0	$10^3 K_A$	$100 \sigma \Lambda / \Lambda_0$
Cosolvent	(S. cm ² .mol ⁻¹)	dm ³ .mol ⁻¹)	(%)
N, N-Dimethylformamide + Water			
0	382.00 ± 0.05	0.724 ± 0.001	0.020
10	301.65 ± 0.01	1.017 ± 0.005	0.008
20	224.87 ± 0.04	1.197 ± 0.007	0.021
30	159.64 ± 0.09	1.330 ± 0.007	0.015
40	100.77 ± 0.02	1.632 ± 0.011	0.009
50	73.15 ± 0.02	2.859 ± 0.012	0.005
60	62.62 ± 0.02	7.079 ± 0.023	0.007
70	50.43 ± 0.03	16.255 ± 0.053	0.006
Acetone + Water			
10	318.55 ± 0.006	1.143 ± 0.004	0.036
20	256.20 ± 0.14	2.142 ± 0.001	0.059
30	216.32 ± 0.20	4.314 ± 0.020	0.050
40	163.12 ± 0.20	8.386 ± 0.036	0.027
50	112.54 ± 0.16	13.996 ± 0.055	0.014
60	84.56 ± 0.05	24.003 ± 0.074	0.008
70	67.10 ± 0.10	39.272 ± 0.081	0.005
Acetonitrile + Water			
10	312.12 ± 0.06	0.979 ± 0.002	0.038
20	265.54 ± 0.03	1.786 ± 0.004	0.013
30	222.03 ± 0.05	3.684 ± 0.012	0.013
40	182.56 ± 0.04	7.250 ± 0.024	0.006
50	134.36 ± 0.08	12.320 ± 0.040	0.007
60	94.80 ± 0.05	18.003 ± 0.046	0.005
70	73.99 ± 0.039	28.582 ± 0.061	0.025

w to water) against composition of water + cosolvent mixtures is non-linear. The non-linearity of these plots (Figs. 1 and 2) indicates that in addition to simple electrostatic interactions some specific solute solvent interactions are taking place.

Experimental

The chloroacetic acid (from Merck, extra pure) was recrystallized from ethanol-water mixture, dried under vacuum over P_2O_5 and stored in a desiccator. The m.p. of acid was 62°C.

The solvents were the same as used in previous studies and their purification has been detailed in these papers [8-9]. The fractionally distilled solvents had specific conductance less than 1.3×10^{-8} S-cm⁻¹. Triply distilled water with the

specific conductance less than 10^{-6} S-cm⁻¹ was used for the preparation of binary mixture and as an aqueous medium. Conductance measurements were carried out using an automatic Microprocessor Conductivity Meter model LF 2000 (Germany) which works at 1kHz. The conductance cell was the same as detailed earlier [8-9]. Two platinized platinum electrodes with cell constant (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 [10] using aqueous KCl solution. The concentrations (molar) 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 25 ± 0.01 °C.

The densities (ρ), viscosities (η) and dielectric constant, ϵ , values for solvent mixtures were taken from literature [8-9]. Other procedure was the same as detailed earlier [8-9]. The physical properties of different solvent mixtures are given in Table 1.

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