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CONDUCTIVITIES AND IONIC ASSOCIATION OF SODIUM PERCHLORATE AND SODIUM BENZOATE IN MIXED SOLVENT SYSTEMS AT 25°

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Electrolytic conductivity measurements have been made on solutions of sodium perchlorate and sodium benzoates in binary mixtures of water with methanol and acetonitrile at 25°. The limiting molar conductivities and association constants were derived from the experimental data with the Fuoss conductivity equation. Sodium benzoate has been found more associated than sodium perchlorate in both solvent systems. The results are discussed in terms of solvent effect on the conductivity parameters as the composition of water + co-solvent mixtures was varied.

Key words: Conductivity, Sodium perchlorate, Sodium benzoate.

Introduction

Sodium perchlorate has been popular supporting electrolyte in the studies of ionic equilibria [1-3] and sodium benzoate has been used for preparation of buffer solutions for the calibration of pH meters both in aqueous as well as in mixed solvent systems [4-6]. Further, sodium benzoate is of special use in beverages and conservation of food stuff.

Present paper is in continuation of the series of electrolytic measurements on these two salts in different binary mixed solvent systems [7-8]. The electrolytic conductivity measurements have been made on sodium perchlorate and sodium benzoate dilute solutions in binary mixtures of water with methanol and acetonitrile at 25° respectively. The conductivity - concentration data were analyzed with Fuoss conductivity equation for the derivation of limiting molar conductivities (Λ_o) and association constant {K_A} values. Finally the results are compared with those available in literature in analogous media and are discussed on the basis of solvent effect on the ionization of these electrolytes as the composition of water + co-solvent mixtures was varied.

Experimental

Chemicals. The salts and acetonitrile were reagent grade of high purity from E. Merck. The salts were dried and kept in a dessicator over P_2O_5. The methanol and acetonitrile were also from E. Merck with 99.8% purity and were further purified as described elsewhere [9-10].

Conductance measurements. The conductance measurements were carried out using a Microprocessor Conductivity Meter model LF 2000 (Germany). Conductivity cells with cell constants (0.011 ± 0.001) and (0.665 ± 0.001) cm^{-1}, respectively were used. Platinized platinum electrodes were used in the cells. The conductivity cell was calibrated following the method of Wu *et al.* [14], using aqueous KCl solutions. Dry nitrogen gas was used for deareation. Other procedure and details have been reported in previous papers [9-13]. The conductivity cell was kept in an oil bath and the temperature of the bath was maintained at 25 ± 0.01°.

The densities ρ, viscosities η and dielectric constant ε, values were taken from literature [11,13].

Results and Discussion

The molar conductances of sodium perchlorate and sodium benzoate solutions of different concentrations in different methanol + water and acetonitrile + water mixtures are given in Tables 1 - 4, respectively. The experimental data were analyzed with Fuoss (1978-80) conductivity equation [15]. The conductivity equation and details of analysis are reported elsewhere [9-13].

The derived conductivity parameters i.e. the molar conductivities at infinite dilution, Λ_o, the standard deviation $\sigma(\Lambda)$ and association constants K_A values for sodium perchlorate and sodium benzoate in different solvent mixtures are collected in the Tables 5-6, respectively. The ion-pair distance parameter for sodium perchlorate was found to be 11 ± 2Å and for sodium benzoate as 7±2Å, respectively for both solvent systems.

The limiting molar conductances. The Λ_o values for both salts in methanol + water mixtures decreased with increase of methanol contents upto 30 mole % composition and then increased. For acetonitrile + water mixtures, the Λ_o values decreased upto 22.7 mole % for sodium perchlorate and 10 mole % solvent mixture for sodium benzoate and then increased as the co-solvent was added to water. The differential behaviour of two different solvent mixtures is due to differences in the structure of water + methanol and water + acetonitrile solvent systems. Methanol is amphiprotic solvent which enhances the water structure on its addition to the latter [16], while acetonitrile is dipolar aprotic solvent which almost

ruptures the water molecular arrangement [17]. The decrease in Λ_o values upto certain composition of water + co-solvent mixture and then increase in these values may be due to differential and preferential solvation of ions with different solvents.

The Λ_o values for sodium perchlorate and sodium benzoate are also available in some acetonitrile + water mixtures in literatue [18-19]. These authors have used different solvent mixtures than those used in present study, therefore an exact comparison between two set of values for these salts could not

TABLE 1. MOLAR CONDUCTANCES, Λ (S. cm^2 .mol^{-1}) FOR SODIUM PERCHLORATE SOLUTIONS IN METHANOL + WATER MIXTURES AT 25°.

	Λ/S. cm^2. mol^{-1}						
X_1 =	10	20	30	40	50	60	70
10^4 C/mol. dm^{-3}							
4.762	93.16	78.17	68.60	65.25	63.40	65.50	72.44
9.091	92.63	77.62	68.04	64.68	62.88	64.73	71.32
13.044	92.27	77.22	67.63	64.26	62.50	64.17	70.50
16.666	91.99	76.90	67.31	63.92	62.21	63.72	69.85
20.000	91.77	76.63	67.04	63.64	61.97	63.34	69.31
23.077	91.59	76.40	66.80	63.40	61.76	63.02	68.84
25.926	91.43	76.20	66.60	63.19	61.56	62.74	68.44
28.571	91.29	76.03	66.42	63.00	61.41	62.48	68.07
31.034	91.17	75.88	66.26	62.84	61.27	62.26	67.75
33.340	91.07	75.74	66.11	62.69	61.15	62.06	67.47
35.483	90.97	75.61	65.98	62.56	61.04	61.88	67.21
37.500	90.88	75.50	65.86	62.43	60.94	61.71	66.97
39.4000	90.81	75.39	65.75	62.32	60.85	61.56	66.76
41.176	90.74	75.29	65.65	62.22	60.76	61.422	66.56
42.857	90.67	75.20	65.56	62.12	60.67	61.29	66.37

x_1 = Mass % Methanol.

TABLE 2. MOLAR CONDUCTANCES, Λ (S. cm^2 .mol^{-1}) OF SODIUM BENZOATE SOLUTIONS IN METHANOL + WATER MIXTURES AT 25°.

	Λ/S. cm^2. mol^{-1}						
X_1 =	10	20	30	40	50	60	70
10^4 C/mol. dm^{-3}							
1.191	76.25	69.18	62.86	56.41	54.41	58.50	62.78
2.273	75.91	68.85	62.52	56.06	54.01	58.04	62.11
3.261	75.66	68.61	62.27	55.80	53.72	57.71	61.63
4.167	75.44	68.38	62.03	55.56	53.45	57.39	61.18
5.000	75.25	68.20	61.84	55.36	53.23	57.14	60.82
5.769	75.10	68.05	61.68	55.19	53.04	56.92	60.53
6.481	74.97	67.91	61.53	55.04	52.87	56.73	60.27
7.142	74.85	67.78	61.40	54.91	52.72	56.56	60.03
7.758	74.74	67.67	61.28	54.78	52.58	56.43	59.81
8.333	74.64	67.57	61.17	54.67	52.46	56.26	59.61
8.871	74.53	67.46	61.06	54.55	52.33	56.10	59.40
9.375	74.46	67.39	60.98	54.48	52.18	56.01	59.23
9.848	74.31	67.24	60.82	54.31	52.06	55.79	59.08
10.294	74.25	67.17	60.75	54.24	51.98	55.70	58.95
10.714	74.19	67.11	60.68	54.17	51.90	55.61	58.73

x_1 = Mass % Methanol.

TABLE 3. MOLAR CONDUCTANCES, Λ (S. cm^2 .mol^{-1}) FOR SODIUM PERCHLORATE SOLUTIONS IN ACETONITRILE+MIXTURE WATERS AT 25°.

	Λ/S. cm^2. mol^{-1}							
X_1 =	0	10	20	30	40	50	60	70
10^4 C/mol. dm^{-3}								
5.00	117.16	106.24	105.82	108.32	110.14	112.64	116.97	124.42
9.629	116.53	105.59	105.32	108.75	109.53	111.95	116.05	122.81
13.928	116.05	105.12	104.99	107.38	109.12	111.50	115.42	121.62
17.931	115.69	104.76	104.76	107.10	108.81	111.14	114.92	120.68
21.666	115.38	104.45	104.57	106.97	108.56	110.85	114.54	120.00
25.161	115.14	104.19	104.41	106.68	108.35	110.62	114.22	119.35
28.437	114.92	103.96	104.28	106.52	108.18	110.43	113.98	118.83
31.515	114.72	103.76	104.17	106.38	108.03	110.27	113.78	118.70
34.411	114.55	103.58	104.07	106.26	107.92	110.14	113.63	118.65
37.142	114.38	103.42	103.99	106.15	107.80	110.03	113.52	118.62
39.723	114.25	103.27	103.90	106.05	107.71	109.93	113.44	118.55
42.162	114.13	103.13	103.84	105.96	107.64	109.86	113.39	118.50
44.474	114.02	103.00	103.77	105.89	107.57	109.80	113.35	118.45
46.666	113.90	102.89	103.71	105.81	107.52	109.75	113.32	118.40
48.750	113.79	102.79	103.66	105.71	107.48	109.72	113.27	118.35

x_1 = Mass % Acetonitrile.

be made. However, the findings in terms of general behaviour of these two salts in acetonitrile + water mixture is found the same. Comparison is shown graphically in Fig. 1. The values found by Mariah *et al.* [19] are about 1% higher than those presently found for sodium benzoate. This difference may be due to selection of different conductivity equations and different R (Gurney co-sphere) distance parameter [15].

Association constants. The KA values for sodium perchlorate are less than 10 in all methanol + water mixtures, respectively. While those for sodium benzoate these values are appreciably higher than sodium perchlorate in all solvent mixtures. The values of association constants indicate that the Na^+ and $C_6H_5COO^-$ ions are partially solvent separated and Na^+ and $C1O^-_4$ ions are completely solvent separated. It may be concluded that K_A values increase with incerase of either methanol or acetonitrile contents in these solvent mixtures.

TABLE 4. MOLAR CONDUCTANCES, Λ (S. cm^2 .mol^{-1}) OF SODIUM BENZOATE SOLUTIONS IN ACETONITRILE+WATER MIXTURES AT 25°.

	Λ/S. cm^2. mol^{-1}							
X_1 =	0	10	20	30	40	50	60	70
10^4 C/mol. dm^{-3}								
5.00	81.00	76.39	77.78	77.98	78.50	81.16	82.88	91.00
9.629	80.41	75.70	77.00	77.23	77.63	79.93	81.40	88.42
13.928	79.98	75.18	76.50	76.73	77.13	78.96	80.30	86.41
17.931	79.63	74.76	76.15	76.30	76.68	78.16	79.37	84.78
21.666	79.34	74.37	75.85	76.06	76.28	77.47	78.58	83.44
25.161	79.13	74.09	75.55	75.65	75.95	76.90	77.92	82.29
28.437	78.88	73.81	75.30	75.37	75.64	76.37	77.33	81.32
31.515	78.70	73.55	75.08	75.14	75.36	75.90	76.72	80.49
34.411	78.54	73.35	74.82	74.94	75.13	75.48	76.36	79.78
37.142	78.38	73.14	74.62	74.71	74.91	75.12	75.96	79.16
39.723	78.23	72.95	74.10	74.34	74.71	74.75	75.61	78.64
42.162	78.12	72.77	74.20	74.38	74.54	74.44	75.30	78.18
44.474	78.00	72.60	74.00	74.24	74.36	74.14	75.00	77.78
46.666	77.86	72.45	73.80	74.09	74.21	73.88	74.76	77.44
48.750	77.75	72.32	73.65	73.96	74.07	73.65	74.55	77.14

x_1 = Mass % Acetonitrile.

TABLE 5. CONDUCTANCE PARAMETERS FOR SODIUM SALTS IN METHANOL + WATER MIXTURES AT 25°.

Mole %	Λ_o/(S.cm^2. mol^{-1})	K_A/(dm^3. mol^{-1})	$100\sigma\Lambda/\Lambda_o$
SODIUM PERCHLORATE			
5.89	94.63 ± 0.01	0.73 ±0.01	0.01
12.3	79.58 ± 0.01	2.55 ± 0.13	0.02
19.4	69.89 ± 0.03	4.54 ± 0.21	0.03
27.3	66.68 ± 0.02	5.33 ± 0.22	0.04
36.0	64.85 ± 0.02	6.55 ± 0.42	0.05
45.7	67.34 ± 0.01	7.30 ± 0.88	0.05
56.7	74.94 ± 0.01	8.88 ± 1.11	0.08
SODIUM BENZOATE			
5.8	77.08 ± 0.03	10.85 ± 0.5	0.01
12.3	69.95 ± 0.03	14.87 ± 0.8	0.02
19.4	63.62 ± 0.04	18.88 ± 0.7	0.04
27.3	57.20 ± 0.03	21.03 ± 1.2	0.03
36.0	55.27 ± 0.03	29.18 ± 1.0	0.02
45.70	59.55 ± 0.04	34.76 ± 1.1	0.04
56.7	64.08 ± 0.06	50.26 ± 1.8	0.08

TABLE 6. CONDUCTANCE PARAMETERS FOR SODIUM SALTS IN ACETONITRILE - WATER MIXTURES AT 25°.

Mole %	Λ_o/(S.cm^2. mol^{-1})	K_A/(dm^3. mol^{-1})	$100\sigma\Lambda/\Lambda_o$
SODIUM PERCHLORATE			
0	118.74 ± 0.05	0.69 ±0.11	0.07
4.7	110.43 ± 0.02	0.87 ±0.06	0.03
9.90	107.43 ± 0.02	1.05 ±0.03	0.02
15.90	104.90 ± 0.02	2.54 ±0.06	0.03
22.70	102.19 ± 0.03	4.08 ±0.18	0.04
30.50	110.25 ± 0.05	4.00 ±0.12	0.05
39.90	119.69 ± 0.01	6.70 ±0.18	0.05
50.60	128.60 ± 0.03	7.27 ±0.11	0.11
SODIUM BENZOATE			
0	82.61 ± 0.07	5.05 ±0.03	0.01
4.7	78.09 ± 0.01	8.51 ±0.02	0.03
9.90	79.44 ± 0.04	9.75 ±0.22	0.03
15.90	79.78 ± 0.02	9.99 ± 0.40	0.02
22.70	80.52 ± 0.03	13.78 ± 0.59	0.04
30.50	83.90 ± 0.01	23.91 ± 0.58	0.03
39.90	86.12 ± 0.02	29.72 ± 1.50	0.06
50.6	95.98 ± 0.03	63.10 ± 2.10	0.11

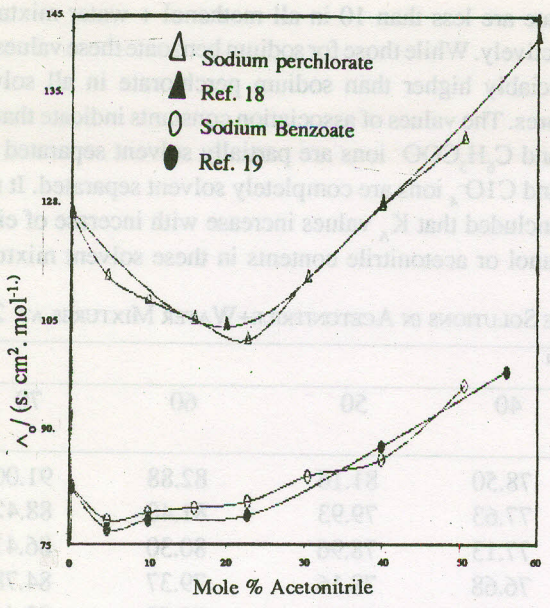

Fig. 1. Comparison of present and literature values.

This may be due to decrease in the values of dielectric constant values of both methanol + water and acetonitrile + water mixtures. As no studies by some other research workers were found in literature for methanol + water mixtures, therefore a comparison could not be made. As seen in the Tables 5 and 6, the solvent composition is effecting differently on each electrolyte in each solvent system.

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