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Conductometric Study on Sodium Perchlorate and Sodium Benzoate in Binary Mixtures of 1-Propanol + Water at 298.15 K

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The eletrolytic conductivities of $NaClO_4$ and C_6H_5COONa have been measured in binary mixtures of water with 1-propanol up to 41 mol % 1-propanol at 298.15 K. The limiting molar conductivities and association constants were derived from the data using the Fuoss (1978–80) conductance equation. The results are discussed in terms of solvent composition.

Introduction

Sodium perchlorate ($NaClO_4$) has been of particular use for maintaining the ionic strength in both aqueous and mixed solvent systems (*1–3*). Sodium benzoate is used as a preservative in beverages and foodstuff.

In two previous papers (*4, 5*), the association behavior of these salts was reported in aqueous mixtures of acetonitrile, *N,N*-dimethylformamide, and tetrahydrofuran. The present paper reports molar electrolytic conductivities of these salts in mixtures of water with up to 41 mol % 1-propanol.

Experimental Section

(*a*) *Chemicals.* 1-Propanol (E. Merck, 99.5%) was further distilled according to the recommendation of IUPAC (*6*). $NaClO_4$ and C_6H_5COONa were the same as used in previous studies (*4, 5*) and were kept in a desiccator containing P_2O_5.

(*b*) *Conductance Measurements.* The conductance measurement was carried out using a Microprocessor Conductivity Meter Model LF 2000 (WTW Germany), which works at the frequency of 1 kHz with an accuracy of 0.01% in conductivity. The cell, electrodes, and procedure were the same as detailed earlier (*4, 5*). The conductivity cell was calibrated using aqueous KCl solutions as recommended by Wu et al. (*7*). The temperature of the oil bath was kept at 25 ± 0.01 °C.

The densities, ρ, viscosities, η, and dielectric constants, ϵ, for the solvent mixtures were taken from a previous paper (*8*), and are given in Table 1.

Table 1. Densities, ρ, Viscosities, η, and Dielectric Constants, ϵ, for x 1-Propanol + (1 − x) Water at 298.15 K

x	ρ/(g·cm^{-3})	η/(mPa·s)	ϵ
0.00	0.9971	0.8903	78.54
0.032	0.9830	1.335	71.80
0.061	0.9672	1.846	64.90
0.115	0.9475	2.227	57.70
0.161	0.9273	2.470	50.30
0.230	0.9060	2.656	43.00
0.311	0.8843	2.669	36.60
0.411	0.8642	2.586	30.70

Table 2. Molar Conductivities, Λ, for $NaClO_4$ in x 1-Propanol + (1 − x) Water at 298.15 K

10^4c/(mol·dm^{-3})	Λ/(S·cm^2·mol^{-1})						
	x = 0.032	x = 0.06	x = 0.115	x = 0.161	x = 0.230	x = 0.311	x = 0.411
9.523	89.75	72.61	61.40	53.40	43.69	39.20	34.88
18.182	88.90	71.71	60.45	52.42	42.59	37.92	33.40
26.864	88.25	71.04	59.74	51.69	41.79	36.98	32.36
33.333	87.72	70.49	59.16	51.10	41.14	36.24	31.55
40.000	87.28	70.03	58.67	50.60	40.61	35.63	30.91
46.155	86.90	69.63	58.25	50.17	40.16	35.13	30.38
51.855	86.57	69.29	57.88	49.80	39.77	34.70	29.93
57.142	86.27	68.98	57.76	49.47	39.43	34.33	29.54
62.068	86.01	68.71	57.26	49.18	39.14	34.01	29.21
66.666	85.77	68.46	57.00	48.92	38.87	33.72	28.91
70.966	85.56	68.24	56.78	48.68	38.64	33.46	28.65
75.000	85.36	68.04	56.54	48.47	38.42	33.23	28.42
78.786	85.18	67.82	56.34	48.28	38.22	33.02	28.22
82.352	85.01	67.67	56.16	48.10	38.04	32.83	28.03
85.714	84.86	67.51	55.99	47.94	37.86	32.67	27.86
88.888	84.71	67.37	55.83	47.79	37.72	32.50	27.70
91.889	84.58	67.23	55.69	47.66	37.58	32.35	27.56
94.736	84.48	67.10	55.56	47.52	37.46	32.23	27.43
97.437	84.39	66.98	55.44	47.40	37.33	32.17	27.31
100.00	84.32	66.87	55.33	47.28	37.17	32.07	27.19

Results and Discussion

The molar conductivities of $NaClO_4$ and C_6H_5COONa solutions of different concentrations in different 1-propanol + water mixtures are given in Tables 2 and 3, respectively.

The experimental data were analyzed using the Fouss (1978–80) conductance equation (*9, 10*). The computer program was the same as the Fuoss scan program and was kindly supplied by Dr. Gilkerson. The limiting molar conductance, Λ_0, and the association constant, K_A, for the process

$$M^+ + A^- \underset{K_a}{\overset{K_A}{\rightleftarrows}} M^+A^- \tag{1}$$

were deduced from the set of equations

$$\Lambda = \alpha[\Lambda_0(1 + \Delta X/X) - \Delta\Lambda_{e1}] \tag{2}$$

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

$$-\ln \gamma = \beta \mathbf{k}/2(1 + \mathbf{k}R), \quad \beta = e^2/\epsilon kT \tag{4}$$

which minimize the standard deviation, $\sigma(\Lambda)$,

$$\sigma(\Lambda) = \{\sum_{mj}[\Lambda_j(\text{calcd}) - \Lambda_j(\text{obsd})]^2/(n - 2)\}^{1/2} \tag{5}$$

by a least-squares analysis, where $\Delta X/X$ is the relaxation

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Table 3. Molar Conductivities, Λ, for C_6H_5COONa in x 1-Propanol + (1 − x) Water at 298.15 K

	$\Lambda/(S\cdot cm^2\cdot mol^{-1})$						
$10^4c/(mol\cdot dm^{-3})$	$x =$ 0.032	$x =$ 0.061	$x =$ 0.115	$x =$ 0.161	$x =$ 0.230	$x =$ 0.311	$x =$ 0.411
1.191	65.83	54.13	44.18	36.67	31.72	28.20	28.50
2.273	65.49	53.81	43.84	36.27	31.26	27.67	27.93
3.201	65.24	53.59	43.60	35.98	30.91	27.29	27.46
4.167	65.01	53.38	43.36	35.70	30.58	26.91	27.02
5.020	64.82	53.21	43.17	35.46	30.30	26.60	26.67
5.769	64.67	53.07	43.01	35.27	30.08	26.35	26.39
6.482	64.40	52.95	42.87	35.09	29.87	26.12	26.13
7.143	64.29	52.83	42.73	34.93	29.69	25.92	25.90
7.759	64.19	52.73	42.60	34.79	29.52	25.74	25.71
8.333	64.10	52.64	42.51	34.66	29.38	25.58	25.52
8.971	64.01	52.54	42.39	34.52	29.21	25.41	25.33
9.375	63.93	52.47	42.32	34.43	29.17	25.30	25.21
10.214	63.86	52.33	42.16	34.24	28.90	25.07	24.96
10.714	63.80	52.27	42.09	34.15	28.81	24.96	24.84
11.111	63.73	52.21	42.02	34.07	28.71	24.87	24.74
11.487	63.68	52.16	41.96	33.99	28.63	24.78	24.64
11.847	63.62	52.11	41.90	33.93	28.55	24.70	24.55
12.180	63.57	52.07	41.85	33.87	28.48	24.62	24.48
12.500	63.52	51.94	41.75	33.80	28.37	24.55	24.40

Table 4. Conductivity Parameters for Sodium Salts in x 1-Propanol + (1 − x) Water at 298.15 K

x	$\Lambda_0/(S\cdot cm^2\cdot mol^{-1})$	$K_A/(dm^3\cdot mol^{-1})$	$R/10^{-8}$ cm	$100\sigma_\Lambda/\Lambda_0$
		Sodium Perchlorate		
0.032	92.00 ± 0.02	4 ± 0.1	10	0.033
0.061	74.66 ± 0.01	8 ± 0.2	8	0.022
0.115	63.46 ± 0.01	13 ± 1	10	0.026
0.161	55.50 ± 0.01	15 ± 1	8	0.033
0.23	46.07 ± 0.02	25 ± 2	8	0.044
0.311	42.14 ± 0.03	38 ± 2	6	0.055
0.411	38.38 ± 0.03	64 ± 3	9	0.069
		Sodium Benzoate		
0.032	66.58 ± 0.028	14 ± 1	6 ± 2	0.069
0.061	54.76 ± 0.011	23 ± 1	6 ± 2	0.032
0.115	44.83 ± 0.004	36 ± 1	7 ± 1	0.015
0.161	37.40 ± 0.002	63 ± 2	7 ± 1	0.010
0.230	32.59 ± 0.011	102 ± 3	6 ± 1	0.049
0.311	29.18 ± 0.004	146 ± 5	7 ± 2	0.021
0.411	29.71 ± 0.010	186 ± 8	7 ± 2	0.026

field effect and $\Delta\Lambda_{el}$ is the electrophoretic countercurrent. $\mathbf{k}^{-1}$ is the radius of the ion atmosphere, ϵ is the dielectric constant of the solvent, e is the electron charge, k is the Boltzmann constant, R is the Gurney-sphere diameter, α is the fraction of solute present as unpaired ions, C is the molarity of the solution, γ is the activity coefficient, and β is twice the Bjerrum distance *(11)*. The derived results are collected in Table 4. The values of the distance parameter R are those values at which a minimum was obtained in the R against $\sigma(\Lambda)$ plot *(10)*.

(a) Limiting Molar Conductances. Table 4 shows that the limiting molar conductances, Λ, for $NaClO_4$ and C_6H_5COONa decreased with addition of 1-propanol in water. The decrease in Λ_0 values may be attributed to increasing viscosities of 1-propanol + water mixtures (Table 1) and different solvation of the ions. Similar results were not found in previous studies *(4, 5)*. The difference may be attributed to different solvent systems. The values of normalized Walden products are plotted against solvent composition in Figure 1. These values have been found to possess a maximum at about x_1 = 0.08 mole fraction of the cosolvent. This maximum does not conform to the maximum in the viscosity–composition curve, which lies at about x_i = 0.31. The variation of Walden products with composition is indicative of selective solvation of the ions in these solvent mixtures. Due to nonavailability of literature values for the Λ_0 parameter in thse solvent mixtures, a comparison could not be made.

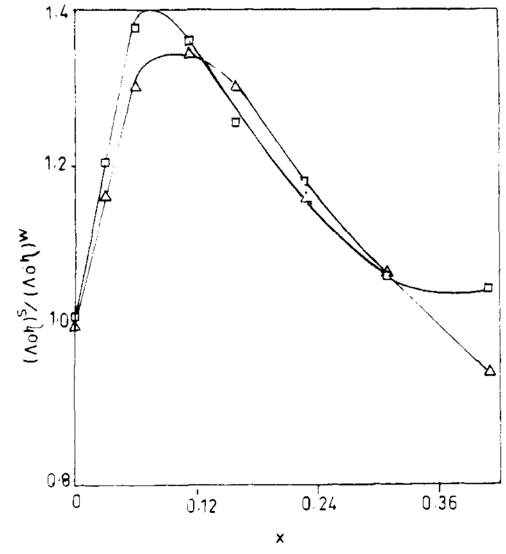

Figure 1. Dependence of normalized Walden products $(\Lambda_0\eta)^s/(\Lambda\eta)^w$ for sodium salts on the composition of x 1-propanol + (1 − x) water at 298.15 K: △, sodium perchlorate; □, sodium benzoate.

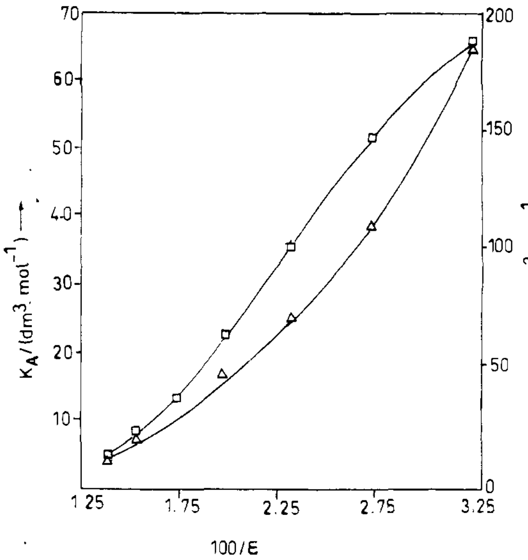

Figure 2. Dependence of K_A values for sodium salts on the inverse dielectric constant values (1/ϵ) for x 1-propanol + (1 − x) water ans 298.15 K: △, sodium perchlorate (left-hand axis); □, sodium benzoate (right-hand axis).

(b) Association Constants. The association constants, K_A, for $NaClO_4$ and C_6H_5COONa in 1-propanol + water mixtures increase with the 1-propanol content (Table 4). Their dependence on 1/ϵ of the solvent mixtures is shown in Figure 2. These plots are nonlinear, which indicates the presence of specific solute–solvent interactions.

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