J. Chem. Eng. Data 1993, 38, 98–100

Conductometric Studies on Sodium Perchlorate and Sodium Benzoate Solutions in Binary Mixtures of Acetonitrile with Water at 298 K

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Conductance measurements have been made on solutions of $NaClO_4$ and C_6H_5COONa in acetonitrile + water at 298.15 K. The limiting molar conductances and association constants were derived from the experimental data by means of the Lee–Wheaton and Fuoss equations. Variations with the solvent composition on the conductance parameters are discussed.

Introduction

A number of studies on binary mixtures of acetonitrile with water have revealed that these solvents mix nonideally and the binary mixture constitutes three distinct regions (*1–3*). This may affect significantly the solvation of ions and ion-pair formation.

Conductometric studies on a number of electrolytes have been carried out in acetonitrile + water (*4–8*). There are only a few studies on $NaClO_4$ and C_6H_5COONa available in some mixtures of these solvent systems (*5, 6*). $NaClO_4$ has been used as an electrolyte for maintaining ionic strength in potentiometry. C_6H_5CooNa also has wide applications.

In the present study, the molar conductances of dilute solutions of $NaClO_4$ and C_6H_5COONa have been measured in acetonitrile + water, ranging in x from 0 to 0.506 of the cosolvent, at 298.15 K. The results have been analyzed in terms of limiting molar conductance (Λ_0) and the association constant (K_A) values, and the results are compared with those available in the literature. Finally the results are discussed on the basis of solvent effects on the ionization of these electrolytes and in terms of solute–solvent interactions.

Experimental Section

(*a*) ***Chemicals.*** The salts and acetonitrile were reagent grade of high purity (99.5%) from E. Merck. The salts were dried and kept in a desiccator over P_2O_5. The acetonitrile was purified as detailed elsewhere (*6*).

(*b*) ***Conductance Measurements.*** The conductance measurements were carried out using a Microprocessor conductivity meter, model L F 2000 (Germany). Conductivity cells with cell constants of 0.011 ± 0.001 and 0.665 ± 0.001 cm^{-1} were used. The platinized platinum electrodes were used in the cells. The conductivity cell was calibrated following the method of Fuoss and co-workers (*11*) using aqueous KCl solutions in the concentration range (2–30) × 10^{-4} $mol{\cdot}dm^{-3}$ with values of conductances of KCl aqueous solutions as recommended by Wu et al. (*17*). The concentrations of $NaClO_4$ and C_6H_5COONa were kept constant for each solvent mixture. Dry nitrogen gas was used to prevent the admission of air into the cell when solvent or stock solution was added to the cell. Other procedures and details have been reported in previous papers (*6, 10*). The conductivity cell was kept in an oil bath, and the temperature of the bath was maintained at 298.15 ± 0.02 K.

The density, ρ, viscosity, η, and dielectric constant, ϵ, values were taken from a previous paper (*6*).

Table I. Densities, ρ, Viscosities, η, and Dielectric Constants, ϵ, for Acetonitrile (1) + Water (2) at 298.15 K

x_1	$\rho/(g{\cdot}cm^{-3})$	$10^3\eta/(Pa{\cdot}s)$	ϵ
0	0.9971	0.890	78.54
0.047	0.9800	0.980	74.66
0.099	0.9586	0.971	70.50
0.159	0.9586	0.912	65.78
0.227	0.9388	0.843	60.20
0.305	0.9135	0.752	55.68
0.399	0.8666	0.657	50.77
0.506	0.8445	0.573	46.52

Results and Discussion

Viscosities and dielectric constants of acetonitrile + water are given in Table I. The molar conductances of $NaClO_4$ and C_6H_5COONa solutions of different concentrations in different acetonitrile + water mixtures are given in Tables II and III, respectively.

The experimental results were analyzed following the method proposed by Pethybridge and Taba which uses the Lee and Wheaton conductance equation (*11, 12*) and that of Fuoss (*13*). The limiting molar conductance (Λ_0) and the association constant (K_A) for the process

$$M^+ + A^- \underset{K_a}{\overset{K_A}{\rightleftharpoons}} M^+A^- \tag{a}$$

were deduced from the equations

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

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

$$-\ln f = \beta k/2(1 + kR) \qquad \beta = e^2/\epsilon KT \tag{3}$$

which minimize the standard deviation σ_Λ

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

by a least-squares analysis. $\Delta X/X$ is the relaxation field effect, and $\Delta\Lambda_{el}$ is the electrophoretic countercurrent. $1/k$ 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, γ is the fraction of solute present as an unpaired ion, C is the molarity of the solution, f is the activity coefficient, and β is twice the Bjerrum distance (*16*).

Conductance measurements can provide at least three parameters: the value of conductance at infinite dilution Λ_0, the value of the association constant K_A, and the ion-distance parameter R that gives the best fit to the conductance equation (e.g., the lowest standard deviation $\sigma(\Lambda)$).

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0021-9568/93/1738-0098$04.00/0

Table II. Molar Conductances, Λ, for Sodium Perchlorate Solutions in Acetonitrile (1) + Water (2) at 298.15 K

	$\Lambda/(\mathrm{S\cdot cm^2\cdot mol^{-1}})$ at various x_1							
$10^4C/(\mathrm{mol\cdot dm^{-3}})$	0.0	0.047	0.099	0.159	0.227	0.305	0.397	0.506
5.00	116.88	108.55	105.82	103.08	99.60	107.94	116.97	125.23
9.629	116.37	107.80	105.32	102.40	98.66	107.33	116.05	123.93
13.928	115.92	107.40	104.99	101.95	97.95	106.91	115.42	123.21
17.931	115.69	107.00	104.76	101.60	97.37	106.60	114.92	122.62
21.666	115.38	106.66	104.57	101.33	96.88	106.38	114.54	122.15
25.161	115.14	106.36	104.41	101.08	96.44	106.08	114.22	121.77
28.437	114.92	106.12	104.28	100.90	96.09	105.89	113.98	121.45
31.515	114.72	105.90	104.17	100.74	95.72	105.72	113.78	121.20
34.411	114.55	105.70	104.07	100.57	95.46	105.57	113.63	120.99
37.142	114.38	105.53	103.99	100.43	95.18	105.40	113.52	120.81
39.723	114.25	105.36	103.90	100.31	94.94	105.30	113.44	120.70
42.162	114.13	105.21	103.84	100.20	94.71	105.19	113.39	120.58
44.474	114.02	105.08	103.77	100.10	94.50	105.10	113.35	120.48
46.666	113.90	104.95	103.71	100.00	94.30	105.00	113.32	120.38
48.750	113.79	104.86	103.66	99.93	94.13	104.92	113.27	120.27

Table III. Molar Conductances, Λ, for Sodium Benzoate Solutions in Acetonitrile (1) + Water (2) at 298.15 K

	$\Lambda/(\mathrm{S\cdot cm^2\cdot mol^{-1}})$ at various x_1							
$10^4C/(\mathrm{mol\cdot dm^{-3}})$	0	0.047	0.099	0.159	0.227	0.305	0.397	0.506
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

Table IV. Conductance Parameters for Sodium Salts in Acetonitrile (1) + Water (2) at 298.15 K

x_1	$\Lambda_0/(\mathrm{S\cdot cm^2\cdot mol^{-1}})$	$K_A/(\mathrm{dm^3\cdot mol^{-1}})$	$100\sigma(\Lambda)/\Lambda$
	Sodium Perchlorate		
0.0	118.74 ± 0.05	0.695 ± 0.11	0.073
0.047	110.43 ± 0.02	0.870 ± 0.06	0.025
0.099	107.43 ± 0.02	1.05 ± 0.03	0.017
0.159	104.90 ± 0.02	2.54 ± 0.06	0.026
0.227	102.19 ± 0.03	4.08 ± 0.18	0.043
0.399	110.25 ± 0.05	4.00 ± 0.12	0.054
0.399	119.69 ± 0.01	6.70 ± 0.18	0.047
0.506	128.60 ± 0.03	7.27 ± 0.11	0.110
	Sodium Benzoate		
0.0	82.61 ± 0.07	5.05 ± 0.03	0.013
0.047	78.09 ± 0.01	8.51 ± 0.02	0.007
0.099	79.44 ± 0.04	9.75 ± 0.22	0.011
0.159	79.78 ± 0.02	9.99 ± 0.10	0.004
0.227	80.52 ± 0.03	13.78 ± 0.19	0.013
0.305	83.90 ± 0.01	23.91 ± 0.11	0.021
0.399	86.12 ± 0.02	29.72 ± 0.11	0.027
0.506	95.98 ± 0.01	63.10 ± 0.10	0.102

In this study no sharp minima in the $\sigma(\Lambda)$ against R plots were observed. For systems where the extent of ion association is small, the analysis of the conductance data using curve-fitting procedures shows the existence of a wide range of R and K_A pairs giving almost equal fit to the experimental data (*14*). The effects on Λ of the nonconducting ion pairs are opposite those of higher terms of long-range forces. Increasing R shifts a calculated conductance curve upward, while increasing association shifts it downward. The consequence of the two opposing effects of the two parameters results in a band of paired values, all of which reproduce the data well. In order to treat data for which the $\sigma(\Lambda)$ against R plot does not show a sharp minimum, the R value is assumed to be $R = a + d$, where a is the sum of crystallographic radii (for $NaClO_4$ and C_6H_5CooNa, the values of a were taken as 2.96 and 2.31 Å (*5, 15*), respectively) and d is given by the formula (*13*)

$$d/\text{Å} = 1.183(M/(\mathrm{g\cdot mol^{-1}}))/(\rho/(\mathrm{g\cdot cm^{-3}}))^{1/3} \qquad (5)$$

where M is the molecular weight of the solvent and ρ its density. For mixed solvents M is replaced by the mole fraction average molecular weight of the mole fractions:

$$M_{av} = M_1M_2/(w_1M_2 + w_2M_1) \qquad (6)$$

where w_i is the mass fraction of component molecular weight M_i.

The molar conductance at infinite dilution Λ_0, standard deviation $\sigma(\Lambda)$, and association constants K_A from the experimental data by means of the Lee–Wheaton equations are listed in Table IV. The Λ_0 values derived using the Fuoss equation were almost the same as those derived by the Lee–Wheaton equation within ±0.11%; therefore, only one set of values is included in the table. The values of R were from 6.5 to 10.5 Å. No association constant values were found for $NaClO_4$ from the analysis of data using the Fuoss equation for all the acetonitrile + water mixtures up to the values of R = 10.55 Å, while some K_A values have been found using the Lee–Wheaton equation, and these are included in Table IV. The conductance parameters for C_6H_5COONa, included in Table IV, were only derived using the Lee–Wheaton equation. The Fuoss equations also gave the same value for Λ_0 and smaller or almost no K_A values for the salt in acetonitrile + water mixtures up to 39 mol % of the cosolvent.

(*a*) ***Limiting Molar Conductances.*** The Λ_0 values for both salts in acetonitrile (1) + water (2) decreased with an increase of the contents up to x_1 = 0.227 for $NaClO_4$ and x_2

= 0.10 for C_6H_5COONa, respectively. Then these values increased with addition of more acetonitrile in these solvent mixtures. Morinaga et al. (*4*) have reported Λ_0 values for $NaClO_4$ in some acetonitrile + water mixtures, and they have also found the similar conductance behavior for this salt in the same solvent system. For an aqueous medium we have found a Λ_0 value of 118.74 $s\cdot cm^2\cdot mol^{-1}$; their value is 119.0 and that of Aprano (*15*) is 117.3. Since our solvent mixtures are different from those of Moriniga et al. (*4*), exact comparison of the Λ_0 values could not be made. C_6H_5COONa have also been studied conductometrically by Manaiah et al. (*7*). They have reported a Λ_0 value of 82.31 $s\cdot cm^2\cdot mol^{-1}$ in water; our value is 82.61 ± 0.07 $s\cdot cm^2\cdot mol^{-1}$. Our values for the Λ_0 parameter for this salt in solvent mixtures of composition 4.7, 9.9, 22.7, and 39.9 mol % acetonitrile are about 1% higher than the values found by them. This difference may be due to selection of a different conductance equation and different R parameter. But the conductance behavior of the salt is the same in both studies.

(*b*) ***Association Constants.*** The K_A values found for $NaClO_4$ are less than 10 in all acetonitrile + water mixtures, while those for C_6H_5COONa are appreciably higher than $NaClO_4$ in all solvent mixtures (see Table IV). $NaClO_4$ is almost completely dissociated in solvent mixtures of composition up to $x = 0.305$ of acetonitrile while C_6H_5COONa has been found associated. The values of association constants indicate that the Na^+ and $C_6H_5COO^-$ ions are partially solvent separated and Na^+ and ClO_4^- ions completely solvent separated in all the solvent mixtures. Comparing the K_A values for C_6H_5COONa presently found and those reported by Manaiah et al. (*5*), it is found that our values are higher. This again is due to differences in the equation and method of analysis. The K_A increase with the increase of the contents of acetonitrile in these solvent mixtures.

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Received for review April 20, 1992. Revised July 15, 1992. Accepted August 3, 1992. Financial support from the University Research Fund (URF) is gratefully acknowledged.