# Conductometric Studies on Sodium Perchlorate and Sodium Benzoate Solutions in Binary Mixtures of Acetonitrile with water 25°C

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## Introduction

A number of studies on binary mixture of acetonitrile (ACN) with water (W) have revealed that these solvent mix non-ideally 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 ACN - W mixtures [4-8]. A few studies on $NaClO_4$ and $C_6H_5COONa$, are available in some mixture of these solvent systems [5-6]. $NaClO_4$ has been used as an electrolyte for maintaining constant ionic strength [6a] in potentiometry. Similarly, $C_6H_5COONa$ has also wide applications as a preservative and is used in beverages.

In the present study, the molar conductances of dilute solutions of $NaClO_4$ and $C_6H_5COONa$ have been measured in (ACN - W) mixtures ranging in mole composition from 0 to 50 % (w/W) of the cosolvent at 25°C. The data have been analyzed in terms of limiting molar conductance ($\Lambda_o$) and association constant ($K_A$) and the results have been compared with those available in [4]. Finally the results are discussed on the basis of solvent effect on the ionization of these electrolytes and in terms of solute - solvent interactions.

## Results and Discussion

The molar conductances of $NaClO_4$ and $C_6H_5COONa$ solutions of different concentrations in different ACN - W mixtures are given in Table 1 and 2, respectively. The experimental data were analyzed according to the method proposed by Pethybridge and Taba [12] based on the Lee and Wheaton conductance equation [11] and Fuoss [13].

The molar conductance at infinite dilution $A_o$, the standard deviation ($\delta\Lambda$) and association

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Table 1: Molar conductances, Λ, for sodium perchlorate solutions in acetonitrile - water mixture at 25°C

| x = $10^4$C/mol.dm$^{-3}$ | 0.0 | 0.047 | 0.099 | 0.159 | 0.227 | 0.305 | 0.397 | 0.506 |
|---|---|---|---|---|---|---|---|---|
| | Λ/(S.cm$^2$.mol$^{-1}$) | | | | | | | |
| 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 | 115.29 | 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 |
| 46.66 | 113.90 | 104.95 | 103.71 | 100.0 | 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 2: Molar conductance Λ, for sodium benzoate solutions in acetonitrile - Water mixture at 25°C.

| x = 0 $10^4$C/mol.dm$^{-3}$ | 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 |
| 9.269 | 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 = Mole fraction of ACN

Table 3: Conductance parameters for sodium salts in acetonitrile - water mixture at 25°C.

| x | $\Lambda_o$/S.cm$^2$.mol-1) | | KA/dm$^3$mol-1) | | 100 (Λ)/Λ | |
|---|---|---|---|---|---|---|
| | 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 | 28.61 | + 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 |

x = Mole fraction of ACN

constants $K_A$ obtained from the experimental data by means of the Lee - Wheaton eqations are listed in Table 3. The $\Lambda_o$ values derived using the Fuoss eqation were almost the same as those obtained from the Lee - Wheaton equation within ± 0.11 %, therefore only one set of values is included in the Table 3. No association constnat values for $NaClO_4$ could be obtained from the data using the Fuoss equation up to the values of R = 10.55 A° for all the acetonitrile + water mixtures. On the other hand some $K_A$ values have been obtained by the Lee - Wheaton equation and these are included in Table 3. The conductance parameters of $C_6H_5COONa$, included in Table 3 were only derived using the Lee - Wheaton eqation. The Fuoss equation also gave the same value for $\Lambda_o$ and smaller or almost no $K_A$ values for the salt in ACN - W mixtures up to 39 mole % of the cosolvent.

*The limiting molar condutance*

The $\Lambda_o$ values for both salts in ACN - W mixtures decreased with increase of ACN contents up to 22.7 mole % for $NaClO_4$ and 10 mole % for $C_6H_5COONa$, respectively. Above these limits $\Lambda_o$ increased with further addition of ACN. Morinaga *et al* [4] have reported $\Lambda_o$ values for $NaClO_4$ in some ACN - W mixture and obtained compatible conductance behaviour. In aqueous medium at $\Lambda_o$ value of 118.74 S. cm$^2$.mol$^{-1}$ comparable to the ones obtained by Morinaga *et al* and Aprano [15], respectively [Ca 119.0 and 117.3]. Since our solvent mixture differ from those of Moriniga *et al* therefore an accurate comparison of the $\Lambda_o$ values could not made. Manaiah *et al* [5] reported $\Lambda_o$ value of 82.31 S.cm$^2$.mol$^{-1}$ in water, for $C_6H_5$ COONa comparable to our value 82.61 ± 0.07 S.cm.$^2$ mol$^{-1}$. On the other hand our $\Lambda_o$ value in solvent mixtures of composition 4.7, 9.9, 22.7 and 39.9 mole % of acetonitrile, are about 1% higher than their values. This difference may be to selection of different conductance equations and different R parameter. But the overall conductance behaviour of the salt is the same in both studies.

*(b) Association constants*

$K_A$ values for $NaClO_4$ are less than 10 in all ACN - W mixtures, while those for $C_6H_5COONa$ are appreciably higher than $NaClO_4$ in all solvent

mixture (Table 3). $NaClO_4$ is almost completely dissociated in solvent mixture of composition up to 30.5 mole % ACN, 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. It may be concluded that $K_A$ values increase with increase of the ACN contents in these solvent mixtures.

## Experimental

### *(a) 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 acetonitrile was purified as described elsewhere [6].

### *(b) Conductance measurements*

The conductance measurements were carried out using Microprocessor conductivity meter model L F 2000 (Germany). Conductivity cells with cell constants (0.011 $\pm$ 0.001) and (0.665 $\pm$ 0.001) $cm^{-1}$, respectively were used. Platinized platinum electordes were used in the cells. The conductivity cell was calibrated following the method of Fuoss and co-workers [9] using aqueous KCl solutions in the concentration range (2 - 30 x $10^{-4}$) $mol.dm^{-3}$. The concentration of $NaClO_4$ and $C_6H_5COONa$ were kept constant for each solvent mixtures. Dry nitrogen gas was used for deareation. Other procedure 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 25 $\pm$ 0.002°C.

The densitieis, p, viscosities, $\eta$, and dielectric constant values were taken from [6].

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