



ELECTRICAL CONDUCTANCE OF ACETYLCHOLINE PERCHLORATE IN TERT-BUTANOL-WATER MIXTURES AT 25°C

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ABSTRACT

The conductance of acetylcholine perchlorate was measured in tert butanol- water mixtures covering a range of dielectric constant $37 < D < 68.25$ at 25°C. The data was analyzed using the Fuoss-Onsager conductance theory to get Λ° , K_A and a° . The equivalent conductance at infinite dilution, for acetylcholine perchlorate decrease with the decrease of the dielectric constant of the medium. The ion parameter a° (solvation) for the perchlorate decreases with decrease of the dielectric constant. The plot of $\log K_A$ vs $1/D$ was not linear indicating that solvent separated ion pairs in this system is characterized by formation of hydrogen bonding.

INTRODUCTION

Studies on electrolytic conductance of acetylcholine halides and perchlorate solutions in water, and various organic solvents, and binary solvent systems, have been reported recently¹⁻¹³. In this paper was present a study of the conductance of acetylcholine perchlorate in tert-butanol-water mixtures at 25°C in order to throw light on the behavior of this salt in mixed solvents The data is analyzed in an attempt to illustrate the electrolyte- solvent interaction, using the Fuoss-Onsager equation¹⁴. The relation between K_A and the size of anion in the above mentioned medium is discussed.

EXPERIMENTAL

Materials

The acetylcholine perchlorate was purified as reported earlier¹. Purification of tert- butanol (BDH) was reported¹¹⁻¹³. It had a specific conductance of $1 \times 10^{-10} \text{ ohm}^{-1} \text{ cm}^{-1}$ and density of 0.78053 gm/cm^3 . Conductivity water was prepared as reported¹. Its specific conductance was found to be $(5-7 \times 10^{-7}) \text{ ohm}^{-1} \text{ cm}^{-1}$.

Properties of Solvent Mixtures

Densities (d) of the mixtures were determined using 20 ml Pyknometer at 25 ± 0.02 °C. Viscosities (η) were measured using a modified Ubelohde suspended level viscometer with flow time at 25°C of 172.4 s for conductivity water. Dielectric constants (D) of mixtures values were used as reported in the



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literature¹⁵. Dielectric constants, viscosities and densities of experimental solvent mixtures used were interpolated from large-scale plots of their data

Conductance Measurements

An Erlenmeyer cell with bright platinum electrodes was used. Its cell constant was calculated using the Lind, Zwolenik, and Fuoss equation¹⁶ and was found to be $0.05443 \pm 0.43 \%$

A Pye" conductance bridge Model 11700, was used measuring the resistances of the solution at 5 Kc/s,

All solutions were prepared by weight reduced to vacuum. Dilution were carried out successively in the cell by siphoning the solvent using a dispenser.

RESULTS AND DISCUSSION

The results are depicted in table (1). Figure (1) show that Λ_0 for acetylcholine perchlorate in tert-butanol-water mixtures decreases with increasing tert-butanol concentration or in other words with decreasing dielectric constant of the medium. This may be attributed to the fact that the ionic mobilities are hindered and the chance for ion-pair formation becomes more prevailing. It would be expected as a consequence that Λ_0 should decrease with the decrease of the dielectric constant. From table (1) and Figure (2) it is seen that (a°) solvation for perchlorate decrease with decreasing the value of dielectric constant, this trend may be attributed to the formation of strong hydrogen bonds between ion and water molecules which weakens gradually on adding tert-butanol.

Table 1 : The characteristic parameters for acetylcholine perchlorate in tert-butanol-water mixtures at 25°C derived from Fuoss-Onsager equation

| t-Butanol wt% | D | 1000/D | Λ_0 | J | a° | KA | Log KA | σ_a | U |
|---------------------------|-------|---------|-------------|--------|-----------|--------|--------|------------|--------|
| Acetylcholine Perchlorate | | | | | | | | | |
| 14.822 | 68.25 | 14.6520 | 52.658 | 175.70 | 5.64 | 112.61 | 2.0516 | 0.0418 | 4.0606 |
| 18.666 | 65.35 | 15.3022 | 47.326 | 154.11 | 5.06 | 45.41 | 1.6571 | 0.0303 | 3.2403 |
| 25.921 | 58.95 | 16.9635 | 42.548 | 166.45 | 4.83 | 127.29 | 2.1048 | 0.1814 | 4.1374 |
| 37.623 | 47.65 | 20.9864 | 36.060 | 187.90 | 3.92 | 279.56 | 2.4465 | 0.0175 | 5.4447 |
| 49.520 | 37.50 | 26.6667 | 21.369 | 193.60 | 3.53 | 63.26 | 1.8012 | 0.0041 | 2.1164 |

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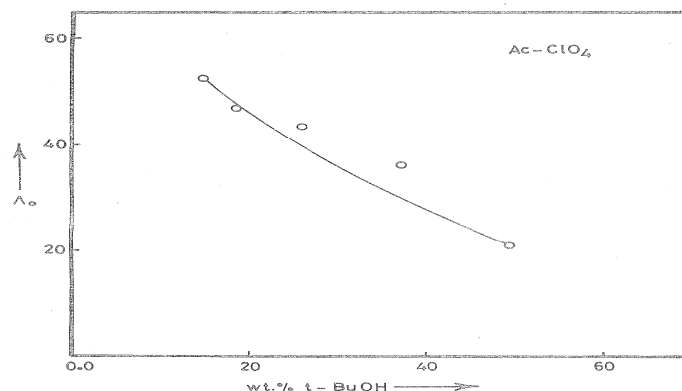


Fig. 1- Variation of Λ_0 with composition solvent mixtures

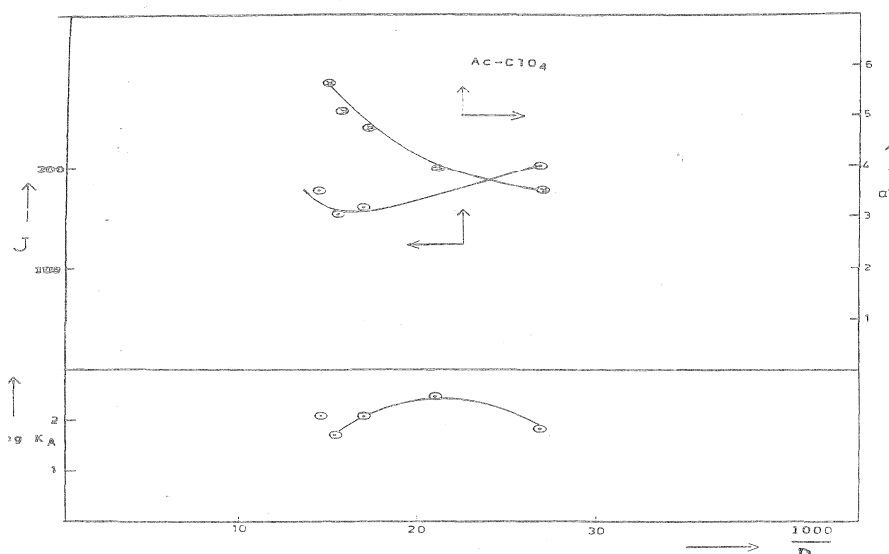


FIG 2 : VARIATION OF α_0 , J AND $\log K_A$ WITH DIELECTRIC CONSTANT OF t-BuOH-H₂O MIXTURES.

The maximum in $\log K_A$ vs. $1/D$ plots for perchlorate in tert-butanol-water mixtures may be explained on the basis that the strength of hydrogen bonds between ion and water are so high to be effected by adding small amount of tert-butanol, i.e., the solvation decreases due to the hydrogen bond formation between tert-butanol and water and hence K_A follows a normal trend.

Thus, the sphere in continuum model cannot be applied to the case of acetylcholine perchlorate in tert-butanol-water mixtures. Further evidence in support this conclusion can be obtained by using the expression¹⁷.



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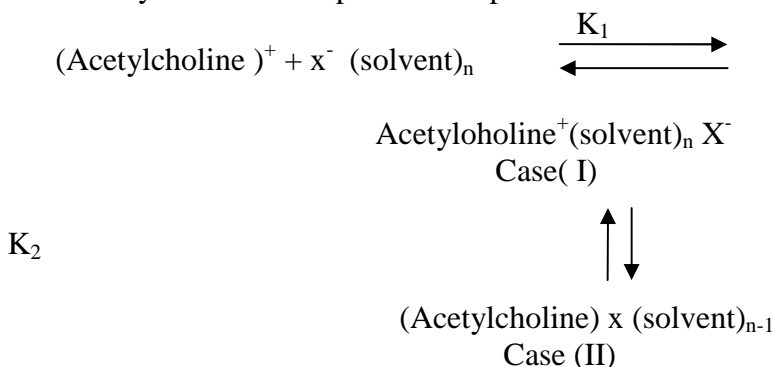
$$\ln K_A = \ln (4 \pi N_A e^3 / 3000) + e^2 / DK T + U$$

Where $U = \Delta S/k - E_s/KT$

The factor E_s/KT introduced by Gilkerson¹⁸ accounts for the ion-dipole interaction energy, which is different when ion-pairs are considered. The entropy term $\Delta S/k$ indicates the change of entropy due to different arrangements of solvent molecules around free ion and ion pairs.

The last column in table (1) shows that U term for acetylcholine perchlorate increases as tert-butanol wt % increase at certain value. This proves that the $\Delta S/k$ (entropy/Boltzmann constant ratio) increases as the dielectric constant of the medium is decreased.

Finally the solvent separated-ion pairs model¹⁹ can be applies as follows:



The association constant is thus given by:

$$K_A = \Sigma K = \frac{(c_{\text{ion-pairs}})}{(c_{\text{Acetylcholine}^+})(c_{\text{X}^- \text{ (solvent)}})} = K_1 (1+K_2)$$

Where; $\Sigma K = K_A$ as obtained from conductance measurements

$$K_1 = 4\pi N_A e^3 / 3000 \epsilon^b$$

From table (2) it is evident that K_2 for acetylcholine perchlorate increase by increasing tert-butanol wt% (i.e. decreasing dielectric constant) till a certain maxim, then decreases again on further additions of tert-butanol, which indicated that the formed ion prefers the more desolvated form (case II) to the completely solvated one (case I). The decrease in K_2 values on further addition of tert- butanol may be explained on all basis that as the tert-butanol wt% increases the ion- pairs prefers the more solvated form (case 1) to desolvated form (case II)



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Table 2 : Estimation of K_2 for acetylcholine perchlorate in tert butanol-water mixtures at 25°C

| t.Butanol wt% | K_A | K_1 | K_2 |
|---------------------------|--------|-------|--------|
| Acetylcholine perchlorate | | | |
| 14.822 | 112.61 | 1.941 | 57.006 |
| 18.666 | 45.41 | 1.778 | 24.542 |
| 25.921 | 127.29 | 2.032 | 61.637 |
| 37.623 | 279.56 | 3.048 | 90.725 |
| 49.520 | 63.26 | 7.621 | 7.301 |

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