

EFFECT OF DIELECTRIC CONSTANT OF MEDIUM ON THE CONDUCTANCE MEASUREMENTS FOR ACETYLCHOLINE HALIDES AND PERCHLORATE AT 25°C

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The conductance parameters, Λ_0 (equivalent conductance at infinite dilution) and K_A (association constant) for acetylcholine chloride, bromide, iodide, and perchlorate in methanol, ethanol, and *n*-propanol at 25°C have been evaluated from the conductance measurements. The values of Λ_0 for different salts decrease with decreasing the dielectric constant of medium (D) in the order MeOH > EtOH > *n*-PrOH, while the association constants of the same salts in different alcohols increase with decreasing the dielectric constant of medium following to the trend *n*-PrOH > EtOH > MeOH.

Key words : Conductance measurement, Acetylcholine halides perchlorate.

INTRODUCTION

Recent theories of the behaviour of electrolytes in solution suggest that the dielectric constant of the medium plays a very important role. Debye and Pauling [1] discussed the various factors that influence the dielectric constant of the medium in the immediate neighbourhood of the ion. It was found that in very dilute solutions the dielectric constant of the pure solvent is the proper value to use for the so-called "Limiting Law" Furthermore, it has been shown that changes of dielectric constant of the medium are closely connected with the corresponding changes of the velocity of homogeneous reactions in solutions. An approach to a theoretical interpretation of the relation of these medium changes to the simultaneous changes in the velocity of certain catalyzed reactions was given by Harned and Samaras [2].

The measurement of dielectric constant [3] of the conducting solutions is still very much a matter of controversy and definite, reliable results seem as yet not to have been obtained. On the other hand, the measurement of the dielectric constant of a pure non-conducting solvent does not offer any particular difficulties and may be carried out by application of a number of different methods. However, even the purest solvent exhibits some conductivity, and the reliability of the measurements decreases rapidly with increasing conductance. Many solvents may act as very weak acids or bases, showing considerable increases of their dissociation constant with increasing temperature and thus also giving less reliable data of their dielectric constant.

Electrolytes in the primary alcohols [4,5] and amides [6] appear to exhibit many of the properties previously observed only in water [7,8] and were attributed to the unique structure of that solvent. In alcohols, ionic associa-

tion was found to increase with anionic size, a result contrary to the prediction of the electrostatic theory. This was interpreted in terms of a multiple-step association process involving hydrogen bonded solvation of anions in the homologous series methanol through 1-pentanol.

EXPERIMENTAL

Purification of salts. The acetylcholine chloride, bromide, iodide, and perchlorate were purified as reported in the literature [9-12].

Purification of alcohols. Methanol (BDH), ethanol (BDH), and *n*-propanol (combrin chemical) were purified as previously reported [10-12]. The specific conductance for MeOH, EtOH, and *n*-PrOH were found to be (4.7×10^{-7}); ($5.4 - 9.6 \times 10^{-8}$), and ($2.3 - 4.8 \times 10^{-8}$) ohm⁻¹ cm⁻¹, respectively.

Properties of solvents. Densities (d) of the alcohols were determined using a 20 ml Pyknometer at 25°C ± 0.02°C and were found to be 0.78657 g ml⁻¹ for *n*-propanol at 25°C.

Viscosities (η) were measured using a modified Ubbelohde suspended level viscometer with flow time at 25°C of 172.45 for conductivity water, and were found to be 0.5448 cp for methanol, 1.0840 cp for ethanol, and 1.9520 cp for *n*-propanol at 25°C.

Values of the dielectric constants were taken after Vidulich and Kay [13] measured the absolute dielectric constant of those solvents in the completely guarded three-terminal dielectric cell using the general radio type 1615 A transformer bridge. The cell constant (2.2 pf), was determined by measurement then corrected to vacuum. All measurements were carried out at 10 kHz.

Conductance measurements. An Erlenmeyer conductivity cell with bright platinum electrodes was used. Its cell constant [9] was $0.05443 \pm 0.43\%$ as calculated using the Lind, Zwolenik and Fuoss [14] equation.

A "Pye" conductivity bridge, Model 11700 was used for measuring the conductance of solutions at 5 Kc/s. All measurements were carried out at $25^{\circ} \pm 0.02^{\circ}$ using water thermostat.

Preparation of solutions. All solutions were prepared by weight reduced to vacuo. Salts are weighed by difference on a microbalance which reads to ± 0.1 mg. Dilutions were carried out successively into the cell by siphoning the solvent by means of a dispenser.

RESULTS AND DISCUSSION

It can be readily seen from Table 1 that the equivalent conductances at infinite dilution (Λ_{∞}) of acetylcholine halides and perchlorate decrease with decreasing the dielectric constant of medium, while the ionic mobilities of ions decrease with decreasing the dielectric constant of medium in the order $\text{MeOH} > \text{EtOH} > n\text{-PrOH}$.

Table 1. Comparison between Λ_{∞} and K_A in different alcohols [10-12] at 25°

Name of salt	Methanol		Ethanol		<i>n</i> -Propanol	
	Λ_{∞}	K_A	Λ_{∞}	K_A	Λ_{∞}	K_A
Acetylcholine Cl	97.03	11.63	42.05	61.50	20.51	174.18
Acetylcholine Br	100.98	27.38	44.60	65.46	22.36	194.68
Acetylcholine I	107.09	18.79	47.37	56.87	23.87	361.81
Acetylchoine ClO_4	114.42	36.23	52.05	106.32	27.19	765.76

The association constants of acetylcholine halides and perchlorate increase with decreasing the dielectric constants of medium in the order $n\text{-PrOH} > \text{EtOH} > \text{MeOH}$, where the association constant increase with increasing the anionic size in each alcohol following the order $\text{ClO}_4^- > \text{I}^- > \text{Br}^- > \text{Cl}^-$. The prediction of the electrostatic theory that the association of an electrolyte in a solvent containing hydroxy groups appears to increase with ionic size. Analysis of the concentration dependence of conductance in methanol solutions gives association constants for alkalimetal and tetra-alkylammonium halides which increase as the size of the anion increases [15]. For example, constants of 0, 4, and 18 have been obtained for tetra-alkylammonium chloride, bromide, and iodide, respectively [4].

Recent studies of Kay and co-workers on the conductivity of several alkylammonium halides in methanol and

ethanol [4-15] have clearly supported our findings concerning the influence of solvent on the association of ion-pairs.

Hafez, *et al.*, [16] found that Λ_{∞} for *s-n*-alkyl-iso-Thiuronium bromides, iodides, and picrates in ethanol *n*-propanol, and *n*-butanol decreases their while K_A increases with decreasing the dielectric constant of medium.

El-Hammamy, *et al.*, [17] found similar behaviour for Λ_{∞} and K_A values for *N-N'*-diphenyl-*s-n*-alkylisothiuronium bromides in methanol, ethanol, *n*-propanol. The decrease of Λ_{∞} is attributed to decrease in ion mobility, while the increase of K_A may be due to the increase of the number of non-conducting pairs in the cosphere.

The effect of solvent is two fold (a) it can stabilize the pairs due to the hydrogen bond chains in the alcohol (b) it can solvate anions by hydrogen bonding [18] so that the expected K_A values is increase.

The participation of alcohols in the ion-pair formation equilibrium, therefore, should involve both steric effect and coulombic effects. On the basis of this approach the structure modifications of the alcoholic polymers generated by added solvents should results in a variable influence of the alcohol molecules on the ion-pair association of electrolytes.

When the higher alcohols are chosen as the solvent system the pattern of ionic association of hydroxy solvents may be investigated without such complications as three-dimensional structural effects or small association constant [4]. Consequently, the K_A values in mixed solvents should vary with the mixture composition in different way from that expected on the basis of the short range ion-ion interactions which depend only on the dielectric constant of the solvent.

The association constant should be only a function of the dielectric constant; their values increase with decreasing the dielectric constant of medium. This is found to be true in studying the behaviour of acetylcholine halides and perchlorate in methanol, ethanol, and *n*-propanol. The association constant was also found to increase with increasing the anionic size in each alcohol: this phenomenon is illustrated in Table 1. The same behaviour of Λ_{∞} and K_A was obtained for tetrabutylammonium halides and perchlorate in different alcohols at 25° [4-15] and is illustrated in Table 2.

A theoretical introduction was written to illustrate the relation between K_A and dielectric constant. It was found that K_A increases as the dielectric constant decreases. This is explained on the basis that the ionic mobility decreases as the dielectric constant decreases and hence the chance to form ion-pairs increases.

Table 2. Comparison between Λ_0 and K_A in different alcohols at 25° for tetrabutylammonium halides and perchlorate [4-15].

Name of salt	Methanol		Ethanol		<i>n</i> -Propanol	
	Λ_0	K_A	Λ_0	K_A	Λ_0	K_A
Bu ₄ NCl	91.38	0	41.54	39	12.16	149
Bu ₄ NBr	95.37	2.6	43.31	75	22.92	266
Bu ₄ NI	101.72	15.6	46.56	123	24.60	415
Bu ₄ NClO ₄	—	—	—	—	27.13	769

From the above picture of the variation of both Λ_0 and K_A with dielectric constant of alcohols, one may conclude that the sphere in continuum model cannot be applied to these systems. Kay and his co-workers [15] studied some salts of the tetra-alkylammonium in methyl alcohol. They obtained values of K_A higher than those expected by using the Bjerum-Fuoss theory [19]. They explained their results on the hypothesis that the ion-pair association is affected by the particular structure of the alcohol.

It can be readily seen from Table 3 that, the association constant would be expected to increase with decreasing cation size, in the order CsI > RbI > KI > NaI. The values of K_A in Table 3 show the reverse dependence. This

Table 3. Conductance data for some alkali metal salts [20,21] at 25°.

Name of salt	Methanol		Ethanol		<i>n</i> -Propanol	
	Λ_0	K_A	Λ_0	K_A	Λ_0	K_A
NaI	108.51	12.8	47.57	55.8	24.38	191.9
KI	115.51	13.2	50.70	81.9	26.31	350.2
RbI	119.68	18.0	52.18	105.4	26.99	472.0
CsI	124.22	23.1	53.63	140.5	27.72	646.4

can be explained by adopting the Lee and Wheaton [20,21] assumption, namely, the formation of solvent-separated ion pairs.

Lee and Wheaton [20,21] obtained similar behaviour for alkali iodides in different alcohols at 25°, i.e., the association constants were found to increase as the dielectric constant of medium decreased according to the trend *n*-PrOH > EtOH > MeOH. While Λ_0 decreased with decreasing the dielectric constant of medium. In conclusion therefore, the ionic mobilities decrease with decreasing the dielectric constant of medium.

Figure 1. shows the plot of the $\log K_A$ vs. $1/D$. Which is linear as expected from the relation [22].

$$\log K_A = \log K_A^\circ + e^2/aDKT$$

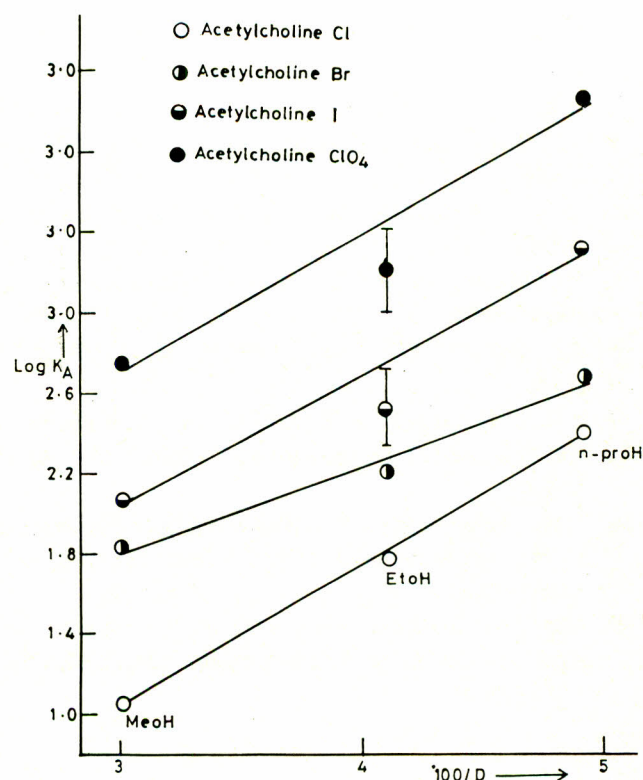


Fig. 1. Variation of $\log K_A$ with dielectric constants for acetylcholine-chloride, -bromide, -iodine, and perchlorate at 25°.

Accasina, *et al.*, [23] studied the conductance of LiClO₃ in dioxane-water mixtures at 25°. They found that in the plot of $\log K_A$ vs. $1/D$, a slight curvature very near to a straight line may be present.

Hafez, *et al.*, [16] measured the conductance of *s-n*-alkylisothiuronium bromides, iodides, and picrates in ethanol, *n*-propanol, and *n*-butanol at 25°. They found that in the plot $\log K_A$ vs. $1/D$ in most cases straight lines were obtained according to the ionic association equation [22]. In other cases a slight curvature may be observed due to the interference of ion-solvent interaction which is proposed by Sadek and Fuoss [24] to amount to $-E_s/KT$.

El-Hammamy, *et al.*, [17] measured the conductance of *N,N'*-diphenyl-*s-n*-alkylisothiuronium bromides in methanol, ethanol, *n*-propanol, and *n*-butanol at 25°. They found that in the plot $\log K_A$ vs. $1/D$ a curvature is observed. This behaviour was explained as being due to solute-solvent interaction.

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