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Variation of Molar Conductance under Isodielectric Condition: A Qualitative Study

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A qualitative study of effect of isodielectric constant on the molar conductance of chloramine-B (CAB) as a function of temperature is undertaken. Reported molar conductance at infinite dilution for chloramine-B obtained by Debye-Hückel-Onsager, Kraus-Bray and Shedlovsky conductivity model are considered in the study. It has been proposed that ion-solvation, *i.e.*, ion-solvent and solventsolvent interaction, the solvent molecular size, its viscosity and other related physical property of the solvent in presence of water are taking major role in molar conductance study keeping effect of dielectric constant as a subsidiary factor.

INTRODUCTION

Conductance studies of electrolytes in mixed solvents have received considerable attention in recent years[1]. It has also been found that the dielectric constant of the medium plays a very important role concerning the behaviour of electrolytes in solution[2]. The study of variation of conductance with concentrations, viscosity and dielectric constant provides satisfactory informations not only about the behaviour of solutions but also regarding ion-solvent interaction[2, 3].

Chloramine-B (CAB), the sodium salt of N-Chlorobenzene sulphonamide ($C_6H_5SO_2NClNa$) is extensively used as oxidimetric analytical reagent for a variety of purposes[4]. From this laboratory we reported[5–7] molar conductance in various pure solvents and solvent mixtures as a function of temperature. In continuation of our earlier work herein we report the subsidiary effect of isodielectric constant on the molar conductance of chloramine-B.

EXPERIMENTAL

Chloramine-B (CAB) was prepared, purified and standardised as described elsewhere[4–8]. Conductance measurements were made with a digital conductivity meter and with a calibrated dip type conductivity cell (cell constant 0.999 cm^{-1}). All measurements were made in a thermostat maintained at the desired temperature ± 0.01°C. All the solvents were used after purification as specified in literature or standard books.

From the experimental point of view, isodielectric was chosen by mixing different co-solvents with water in appropriate proportions (10% methanol, 10% ethanol, 60% dimethyl sulphoxide at 313 K or 60% ethanol, 80% acetonitrile at 303 K) and by selecting pure solvents (H_2O, MeOH, MeCN, DMSO) of similar dielectric constants, at a given temperature. Solvent of CAB was prepared in these isodielectric mixtures and conductivity was measured. Dielectric constants of various solvent mixtures at different temperatures were selected from literature[9–11].

RESULTS AND DISCUSSION

Molar conductance of CAB at infinite dilution (Λ^{o}_{m}) was determined by different conductivity equations proposed by Debye-Hückel-Onsager, Kraus-Bray and Shedlovsky as described earlier[5, 6] (except in the case of DMSO which is under communication) and hence required and relevant values of different temperature and solvent composition (v/v) are given in Table-1 as a function of isodielectric and temperature. Association constant (K_a) computed by Shedlovsky method, Stoke's radius(r) calculated by Walden equation and relevant values are shown in Table-1.

TABLE-1

COMPUTED VALUES OF MOLAR CONDUCTANCE AT INFINITE DILUTION (Λ^{o}_{m}, ohm^{-1} cm^2 s^{-1}), ASSOCIATION CONSTANT (K_a) AND STOKE'S MOLECULAR RADIUS (r) UNDER ISODIELECTRIC CONDITION (ε) AT DIFFERENT TEMPERATURES

283 K					293 K				
ε	Solvent	Λ^{o}_{m}	K_a	$r \times 10^{-18}$ cm	ε	Solvent	Λ^{o}_{m}	K_a	$r \times 10^{-18}$ cm
37.7	80% EtOH	21	22.8	5.1					
38.3	100% MeCN	73	51.0	9.6	71.0	20% MeOH	69	7.4	3.1
37.5	100% MeOH	62	68.3	6.8	71.8	20% MeCN	64	4.1	3.8
79.6	10% MeOH	62	14.2	3.2	75.6	10% MeOH	84	21.9	2.6
78.5	10% MeOH	52	2.1	3.5	75.0	10% EtOH	68	3.1	3.1
77.6	60% DMSO	18	12.3	3.1	74.2	60% DMSO	22	9.1	3.2
74.8	20% MeOH	54	5.1	3.3	36.7	80% EtOH	26	18.8	4.8
75.4	20% MeCN	74	1.8	4.6	37.5	100% MeCN	84	85.0	8.9
61.5	40% EtOH	26	3.1	3.7					
61.6	50% MeCN	55	6.5	4.6					
303 K					313 K				
45.2	60% EtOH	57	7.2	2.9	43.2	60% EtOH	61	6.7	2.8
44.6	80% MeCN	102	18.3	5.0	43.0	80% MeCN	119	29.2	4.6
44.5	100% DMSO	29	25.6	5.1	68.6	10% MeOH	117	34.1	3.2
55.7	40% EtOH	52	4.5	3.0	68.0	10% EtOH	105	4.4	2.9
56.6	50% MeCN	95	12.2	3.3	67.3	60% DMSO	37	8.2	3.1
71.5	10% EtOH	84	3.8	3.1	53.2	40% EtOH	66	4.9	2.9
75.9	40% DMSO	44	4.2	3.8	54.0	50% MeCN	120	25.8	2.8
					73.0	100% H_2O	110	8.2	3.7
					72.9	10% DMSO	110	13.3	2.7
					77.4	20% DMSO	78	3.1	3.3

As can be seen from Table-1 at a given temperature under isodielectric condition CAB showed variable values for molar conductance at infinite dilution (Λ_m^o). For example, at 283 K, 80% EtOH, 100% MeCN, and 100% MeOH, even though having almost the same effective dielectric constant (isodielectric) Λ_m^o is different. Likewise at 293 K 10% MeOH, 10% EtOH and 60% DMSO even though are iso-dielectric the Λ_m^o is fully different. Similar cases can be seen at 303 K and 313 K. From these it is very clear that mere dielectric constant is not the factor responsible for the conductance of species. It is a well known fact that dielectric constant is a measure of dissociation irrespective of its source. Λ_m^o should be the same at an isodielectric condition. But practically it is not so as shown in Table-1. Qualitatively it may be attributed for the following reasons: The solvent molecular radius, the solvent-solvent interaction, nature of the solvent, its capacity to form hydrogen bonding with other solvent and ions, the dipole moment of the solvent, etc., are responsible for this observed behaviour and also the temperature or thermal energy. Among the solvents under consideration methanol and ethanol are dipolar, protic having same affinity towards proton (protophilic) with better co-ordinating capacity; moreover, they act as structure breaker with water by forming a mixture MeOH/EtOH-H_2O. They also behave like aqueous solvents whereas MeCN and DMSO, even though dipolar and protophilic, are typical non-aqueous (thermodynamically) aprotic and structure-formers with water. The ionic size of solvent decreases in the order of r DMSO > r EtOH > r MeCN > r MeOH > r H_2O > r EtOH. At 283 K, under isodielectric conditions, in 100% MeCN and in 100% MeOH chloramine-B exhibits high Λ_m^o whereas in 80% EtOH Λ_m^o is very small. Here ethanol is a structure-breaker *and protophilic*. Due to this some of the ethanol molecules may go into the cavity of 3-dimensional water structure by breaking the structure and further this complex may solvate the ionic species, or due to the breaking of the bond more solvent may take part in the solvation of the ion, and hence ionic size increases and conductivity relatively decreases. Either at 100% MeOH or 100% MeCN solvent-solvent interaction is fully absent and hence Λ_m^o is invariably higher compared to 80% EtOH. Even though the size of acetonitrile molecule is bigger compared to methanol, its dipole moment is higher. Dielectric constant is marginally high for MeCN. Therefore Λ_m^o is high in 100% MeCN compared to 100% MeOH. It can be proved even on the basis of ion-solvent interaction. Another interesting point to be considered in this case is the association constant (K_a). K_a for 100% MeCN is smaller than 100% MeOH; it means in methanol the ions have undergone more association compared to that in acetonitrile. This is clear from high Λ_m^o in 100% MeCN. But contrarily low value of Λ_m^o in 80% EtOH cannot be explained on the basis of K_a value. Here the solvent-solvent interaction, its high molecular size and small dipole moment value collectively takes important role in exhibiting the minimum value for Λ_m^o under prevailing conditions. Indeed, the role of viscosity is also a considerable fact. At 283 K of course thermal energy is not an important point to be considered, but at 293 K we find abother similar isodielectric state. The increase in Λ_m^o of CAB with temperature (283 to 293 K) indicates the increase in thermal energy and minimum effect of dielectric constant variation. No doubt as the temperature is increased relative ionic size or molecular size decreases and hence the conductivity. This fact[5, 6] is proved by calculated and reported[5, 6] ionic/molecular size using Walden equation[12] value. Stoke's molecular radius calculated from Walden product is decreased as temperature is increased (Table-1). But under single temperature just on the basis of Stoke's molecular radius it is a bit difficult to explain the variation observed in Λ_m^o .

Let us consider another case (which is similar to the one discussed now) of isodielectric state (43 ~ 45) 60% EtOH, 80% MeCN at 303 K and 313 K and 100% DMSO at 303 K. Here one finds slight decrease in dielectric constant with increase in temperature by 10 K. But the increase in Λ_m^o from 303K to 313 K is purely due to rise in temperature or thermal energy or decrease in viscosity of the system and other related properties but not because of the changes in dielectric constant. It may also be due to high molecular size and low dipole moment value of ethanol than acetronitrile. Acetonitrile has less ordered bulk structure as compared to water. Dimers of acetonitrile are detected only in pure solvent but not in solvent mixture and hence as such negative charge centre of N-atom of acetonitrile is not available resulting in the protophobic character. This might have led to lower solvent-solvent interaction. But again contradictory result are obtained if one looks at Λ_m^o value through K_a. But the same K_a can be utilised in case of the value of CAB in 80% MeCN and 100% DMSO at 303 K. Low K_a and high Λ_m^o for 80% MeCN compared to 100% DMSO at that temperature and isodielectric state is due to smaller ion-ion association in 80% MeCN. In 80% MeCN which is co-solvent rich region and hence acetonitrile character is predominating as compared to 60% ethanol (which is middle region) and 100% DMSO where it is free from any solvent-solvent interaction. The Λ_m^o for CAB in 100% DMSO is very less because of higher ion-solvent interaction, larger molecular size and viscosity, and also its self-association nature (due to dipole-dipole interaction unlike in alcohols). Moreover, ions may go inside the cavity formed during self-association of DMSO, making lesser number of ions available for conductance. Similarly variation in Λ_m^o in other isodielectric state can also be discussed.

In case of monohydric alcohols the following facts may also be considered. More basic character of alcohol-water than that of water is due to the inductive effect of methyl group at higher alcohol concentration. Addition of methanol to water initially increases the total basicity of the medium but after a mole fraction of about 0.8 the basicity of the solvent mixture decreases and may fall to a value less than that of water[2,11]. In case of ethanol, strong and well organised ethanol-H_2O hydrogen bonds are formed and in general (R—OH) (H_2O) are also detected at higher concentrations. Not only this, even solvent visosity is also taking major role in the mobility of ions.

Interaction of chloramine-B ($C_6H_5SO_2NClNa$) species, *i.e.*, $C_6H_5SO_2NCl^-$ and Na^+ with different solvents in presence of water is also an important factor to be considered since chloramine-B provides different species[4], at different pH. The pH of water-alcohol varies as the alcohol contents increase as stated above.

In general it may be stated that although in a few solvent mixtures the concentration is a linear function of composition, and hence the conductance, this is not true in all cases and the mixtures of a hydrogen-bonding solvent with a non-hydrogen bonding solvent can be particularly non-ideal in this regard. The solvent or solvent mixture affects conductance primarily through its viscosity, its dielectric constant and its specific interaction with ions, and solvent viscosity resists the motion of ions. The dielectric properties of the solvent control the effective field strength and their ionic potential. These affect not only ion viscosity, but also the attraction between ions, and consequently the extent of pairing. Specific solvation of ions can affect both mobility and association.

From these it may be concluded that the dielectric constant of any solvent or solvent mixture is not at all sufficient to explain the observed conductance behaviour of any electrolyte. It can give only a supporting evidence in regard to conductance. High dielectric constant may dissociate polar electrolytes in polar solvents producing ions. This arises a question that what is its interaction with solvent-molecules. But if we take single non-aqueous solvent with water and study the conductance profile it may be possible to correlate a relation between conductance and dielectric constant as we do in kinetics to explain Amis concept, but rarely one would get expected success. It is always a combined effect of solvent-solute, solvent-solvent, ion-solvent, dipole moment, temperature, viscosity and other related and chemical properties.

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