CHAPTER - 6

GENERAL DISCUSSION

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Molar conductance measurements have been carried out for the electrolytes ammonium chloride, dimethyl ammonium chloride and tetramethyl ammonium chloride in ethanol-water, methanol-water and acetone-water mixed solvents at 5, 10, 15, 20, 25 and 30°c. The composition of non-aqueous solvents used were 0, 10, 20, 30, 40, 50, 60, 70, 80 and 90 % (v/v). The concentrations used for ammonium chloride in ethanol-water were $1x10^{-2}$ M, $1x10^{-3}$ M, $5x10^{-4}$ M, $1x10^{-4}$ M and $5x10^{-5}$ M; in methanol-water $1x10^{-2}$ M, $5x10^{-3}$ M and $1x10^{-3}$ M while in acetone-water the concentrations used were $1x10^{-2}$ M and $1x10^{-3}$ M and $5x10^{-4}$ M. The minimum in molar conductance for ammonium chloride is observed at lower concentrations only, therefore dimethyl and tetramethyl ammonium chloride were studied only at $1x10^{-4}$ M, $5x10^{-5}$ M and $1x10^{-5}$ M concentrations for ethanol-water system. The concentrations studied for dimethyl ammonium chloride and tetramethyl ammonium chloride in methanol-wate systems were $1x10^{-2}$ M, $5x10^{-3}$ M, and $1x10^{-3}$ M; $1x10^{-2}$ M, $1x10^{-3}$ M and $5x10^{-4}$ M concentrations studied in acetone-water system.

A minimum in molar conductance have been observed at 5 and 10°c for the concentrations 1 $x10^{-4}$ M and $5x10^{-5}$ M for ammonium chloride in ethanol-water mixed solvents.

There is regular decrease in molar conductance at 15, 20, 25 and 30°c for these concentrations, while for $1x10^{-2}$ M, $1x10^{-3}$ M and $5x10^{-4}$ M concentrations there is no minimum in molar conductance. For dimethyl ammonium chloride minimum in molar conductance is observed only at 5 °c for $5x10^{-5}$ M concentration and 5, 10 and 15°c for $1x10^{-5}$ M concentration in ethanol-water system. Similarly the minimum in molar conductance is observed at 5, 10 and 15°c for $5x10^{-5}$ M and $1x10^{-5}$ M concentrations for tetramethyl ammonium chloride in ethanol-water system.

In the case of methanol-water systems, the minimun in molar conductance has been observed not only at 5, 10 and 15°c but also at higher temperature 20, 25 and 30°c and for all the concentrations studied viz. $1x10^{-2}$ M, $5x10^{-3}$ M and $1x10^{-3}$ M for all the three electrolytes studied.

In acetone-water mixed solvents the molar conductance does not pass through minimum for the concentration $1x10^{-2}$ M even at low temperatures for ammonium chloride and dimethyl ammonium chloride, it has been observed that molar conductance values fall sharply beyond 80 % of acetone. But in the case of tetra methyl ammonium chloride minimum in molar conductance is observed for all temperatures for $1x10^{-2}$ M concentration. A minimum has been observed for all the temperatures studied for $1x10^{-3}$ M and $5x10^{-4}$ M concentration for all the three electrolytes in acetone-water system.

It seems that the minimum in molar conductance, at all temperatures and for all concentrations studied in methanol-water system is due to structure breaking of water and establishment of new hydrogen bonds to form methanol-water clusters for all the three electrolytes. The clustering is favoured only at 5, 10 and 15°c in the case of ethanol-water system and only for concentrations 5×10^{-5} M and 1×10^{-5} M. In the case of acetone-water system the clustering is favoured at all temperatures for the concentrations 1×10^{-3} M and 5×10^{-4} M and for tetra methyl ammonium chloride, clustering is favoured for 1×10^{-2} M concentration also.

In the case of tetra methyl ammonium chloride, it has been observed that the minimum in molar conductance is also observed at higher concentration of 1×10^{-2} M. This may be attributed to the structure-making effect due to tetra-methyl ammonium ion.

When an electrolyte like ammonium chloride is dissolved in mixed solvents such as ethanol-water, ammonium chloride dissociates less and ammonium and chloride ions get attached themselves to water molecules and ethanol molecules. This results to the division of ammonium chloride in water and ethanol. The ions attached to water molecules show very high molar conductance as compared to the ions attached to ethanol molecules and therefore, the ammonium chloride in water mainly contributing towards the conductance. The number of solvent molecules in association with ions should depend upon the composition of solvent mixtures. Hence, as the percentage of non-aqueous solvents increases, the molar conductance decreases.

Molar conductance is dependent on the nature and velocity of ion. Hence, diminution in fluidity of solvent, which would bring about a corresponding decrease in ionic mobility, is an important factor causing the minimum in molar conductance. The change in ionic atmosphere which surrounds the ion is also an important factor in causing the minimum in molar conductance.

An explanation that can be offered to account for the minimum in molar conductance is that in these associated solvents, each solvent diminishes the association of the other, since the dissociating power is a function of the association in the solvent anything that will diminish the association will diminish the dissociating power. The effect of mixing two associating solvents would then dissociate less than either alone and the molar conductance of an electrolyte in such a mixture would be less than that in pure solvent and the molar conductance curve if plotted against the percentage of non-aqueous solvent would pass through a minimum.

When an electrolyte is added in a concentrated form the dielectric constant of medium decreases rapidly with the result that dissociating power of electrolyte in mixed solvent becomes less and molar conductance decrease is observed throughout the entire composition range and therefore no minimum in molar conductance is observed. Martin (1929-34-37), Kirkwood (1934), and Bell (1935) after studying static dielectric constant of alcohol-water mixtures have shown that lowering of static dielectric constant values takes place than the additive values but this can not be related directly to the structural complexities. Hence, lowering of molar conductance in alcohol-water mixtures may not be attributed entirely to the change in the dielectric constant though dielectric constant is one of the important factor that affects the molar conductance.

As temperature is increased the association of mixed solvent decrease because hydrogen bond which exists in between two molecules is broken, this results in decrease in molar conductance continuously throughout the composition range.

Various workers have observed that there is a close relation between conductivity minimum and viscosity maximum. The minima and maxima are more pronounced at lower temperatures and lower concentrations. The static dielectric constant of medium decreases with increase in concentration of non-aqueous solvent. The recent work of viscosity in entire range of acetone-water, ethanol-water and methanol-water mixed solvent shows that viscosity is maximum in the range 40 to 60 percent non-aqueous solvent.

Leu (1979) has shown that viscosity for ethanol-water system is 2.5 times of ethanol or water at 70 % ethanol dilution. Therefore, qualitatively it can be interpreted that the decrease in molar conductance of an electrolyte when dissolved in mixed solvent is partly due to less dissociation (due to decrease in dielectric constant of the solvent) of electrolyte in binary solvent and partly due to increase in the viscosity. However, all these effects need to be explained in terms of structure of mixed solvents. When an alcohol is added to water, the water structure is broken but new hydrogen bonds are established in order to form alcohol-water clusters. These clusters help to decrease the ionic mobility, hence, increase in viscosity and decrease in conductivity of solution. The number of such clusters increase with increasing concentration of ethanol or non-aqueous solvent and if number of clusters is maximum at 70 % ethanol then minimum can be explained.

The systems studied at six different temperatures, indicate that the molar conductance values increase linearly with temperature. This can be seen from the temperature - molar conductance graphs at the end of each system.

The volume contraction of each mixture has been determined while preparing the solutions at 30° c. The volume contraction is maximum in the composition range 40 to 70 % of non-aqueous solvents and it has nearly the same values in this range. This may be the proof of association factor, which causes minimum in molar conductance. The volume contraction is found to be almost the same for ethanol-water and methanol-water. The volume contraction in the case of acetone-water systems is higher than alcohol-water systems. This may be due to more association of acetone and water. The volume contraction is found to be independent of concentration and nature of salt. This can be seen from following table :

Volume contraction of water-ethanol, water-methanol and water acetone with tetramethyl ammonium chloride as a electrolyte at 30°c.

% Non-aqueous solvent	Volume decreases on mixing in ml/250 ml		
	Ethanol	Methanol	Acetone
10	2.2	2.1	2.6
20	4.6	4.6	4.9
30	6.7	6.7	7.3
40	9.1	9.2	9.4
50	9.8	9.7	9.8
60	9.1	9.0	9.2
70	8.9	8.9	9.0
80	7.4	7.4	8.1
90	5.2	5.3	5.8

The study of molar conductance of ammonium chloride in ethanol-water, methanol-water, and acetone-water mixed solvents reveals that molar conductance values obey the order,

acetone-water> methanol-water > ethanol-water

upto 60 % of the non-aqueous solvents. Above this percentage the order changes as :

methanol-water > acetone-water > ethanol-water.

The reasons for the change in order can be attributed to the following factors :

1. The association of acetone-water is higher than alcohol-water.

2. The viscosity of acetone-water medium is lower than methanol-water medium.
3. The static dielectric constant of methanol-water medium is higher than acetone-water.

The study of molar conductance of ammonium chloride, dimethyl ammonium chloride and tetramethyl ammonium chloride in ethanol-water, methanol-water and acetone-water, mixed solvents has revealed that molar conductance values obeys the order :

NH_4Cl > $Me_4N\ Cl$ > $Me_2\ NH_2Cl$

The molar conductance of tetramethyl ammonium chloride is greater than dimethyl ammonium chloride, this may be attributed to the 'structure-making' effect in tetramethyl ammonium chloride due to tetra methyl ammonium ion.