Chapter 6: Summary and Conclusion

6.1 Introduction

6.2 Conductance studies in mixed binary aqueous solvent
   6.2.1 Walden product ($\Lambda_0\eta$) values and ion-solvent interactions
   6.2.2 Ion association, ion-solvent and solvent-solvent interactions
   6.2.3 $\Delta H^0$ values of ion association

6.3 Conductance studies in mixed binary non-aqueous solvents
   6.3.1 Understanding of ion-solvent interactions from Walden product ($\Lambda_0\eta$) and limiting ion conductance values
   6.3.2 Ion association and solvation effects

6.4 Conclusion
6.1 Introduction
The thesis deals with conductometric investigation of ion association and ion solvent interaction in mixed binary aqueous and non aqueous mixtures. Conductance measurements have been carried out in different solvent mixtures at different temperatures (288-308K). The data have been analysed using Shedlovsky’s conductance equation\(^1\). 1-ethyl-4-cyanopyridinium iodide is chosen as a solute for conductance study. The solute is characterised by the existence of different types of ion pairs\(^2,3\) in pure and mixed non aqueous solvents. A systematic analysis of conductance data in mixed binary aqueous and non aqueous solutions at different temperatures have been done to get limiting conductance, \(\Lambda_0\) and association constant, \(K_a\) values in different solvent compositions. The results have been analysed to extract information about ion-solvent and solvent-solvent interactions. The important findings are summarised below.

6.2 Conductance studies in mixed binary aqueous solvents
6.2.1 Walden product \(\Lambda_0\) values and ion-solvent interaction
Walden product \(\Lambda_0\) values have been determined in different solvent composition of mixed-binary aqueous solvents containing ethanol (1) + water (2), acetonitrile (1) + water (2), acetone (1) + water (2) and 1,4-dioxane (1) + water (2) at different temperatures. A representative plot of \(\Lambda_0\) versus mole fraction of ethanol, \(x_1\) for ethanol (1) + water (2) mixtures is shown in the (figure 6.1). It appears from the plot that \(\Lambda_0\) values in general pass through a maximum with the increase of \(x_1\), the position of maximum varies from one solvent system to another. The increase in temperatures for a given solvent composition leads to a decrease of \(\Lambda_0\) values.

The variation of \(\Lambda_0\) values with the solvent composition for a solvent systems reflects the change in solvation of the ions of electrolytic solutions\(^4\). The maximum of \(\Lambda_0\) vs \(x_1\) plot indicates a significant decrease in the total solvation size of the ions. The results have been interpreted in terms of (i) preferential solvation\(^5,6\) by solvent molecules due to solvent-solvent and ion-solvent H-bonding in protic-protic and protic-cyclic ether solvents
Figure 6.1. Plots of Walden product ($\Lambda_0\eta$) and viscosity ($\eta$) as a function of $x_1$, the mole fraction of ethanol in ethanol-water mixtures.

- $\circ$, 293 K
- $\bullet$, 298 K
- $\Delta$, 303 K
- $\Delta$, 308 K.
(ethanol + water and 1,4 dioxane + water). (ii) prevalence of microheterogeneity in the solvent mixtures containing protic and aprotic solvents (acetonitrile + water and acetone + water) in presence of solute.

The negative temperature coefficient of the Walden products has been interpreted as due to the thermal expansion of solvated ions.

6.2.2 Ion association, ion-solvent and solvent-solvent interactions

The conductance data have been analysed using Shedlovsky’s conductance equation. The value of R parameter, the average distance of closest approach of oppositely charged ions, has been calculated using the equation proposed by Fuoss.

\[ R = a + d \]  \hspace{1cm} \text{(6.1)}

Where \( a \) is the sum of crystallographic radii of ions and \( d \) is given by

\[ d = 1.183 \left( \frac{M}{\rho} \right)^{1/3} \]  \hspace{1cm} \text{(6.2)}

In the above equation \( M \) is the average molecular weight of the solvent system and \( \rho \) is its density.

The experimentally determined association constant (\( K_a \)) has been found to increase with \( x_1 \), the mole fraction of non aqueous solvents, showing an increased association as non aqueous solvents is added to water. The significantly large values of \( K_a \) and exothermic ion pair formation in water rich region indicates the presence of specific short range interaction within the ion pair. The phenomenon of ion pair formation due to interplay of electrostatic and short range interaction is represented by the scheme (I).

\[ Si + A^+ + B^- \quad \text{(free ions)} \]

\[ K_R \]

\[ K_{AC} \]

\[ K_{Si} \]

\[ (A^+ \parallel B^-)_i \quad \text{(i-th solvent separated ion)} \]

\[ (A^+, B^-) + Si \quad \text{(contact ion pairs)} \]

\[ K'_{Si} \]

\[ Scheme (I) \]
Here the subscript "i" (i=1,2) refers to the components of the binary solvent mixture involved in the formation of solvent separated ion pair. K's are the equilibrium constants. The experimentally determined association constant, $K_{1}$, according to scheme (I) is given by

$$K_{A}=K_{AC}/[1+K'_{S,2}+(K'_{S,1}-K'_{S,2})x_{1}]$$

...(6.3)

The parameter $K_{AC} = K_{R}K_{S,1}$ can be separated into an electrostatic contribution ($K_{el}$) and specific short range interactions ($K_{sp}$). $K_{el}$ is given by Fuoss equation. By rearranging equation (6.3) we get

$$K_{A}/[(4\pi NR^{2}/3000)\exp(e^{2}/DRkT)]=K_{Sp}[1+K'_{S,2}+(K'_{S,1}-K'_{S,2})x_{1}]$$

...(6.4)

A plot of L.H.S. of equation (6.4) versus $x_{1}$ at different temperatures for different solvent systems are shown in (figure 6.2). The slopes of the curves over the entire mole fraction range of solvent (S1) are determined by the values of $K'_{S,1}$ and $K'_{S,2}$ which incorporate specific short range solute-solvent and solvent-solvent interactions.

In ethanol (1) + water (2) and 1,4-dioxane(1) + water (2) mixture [figure 6.2 (a) and 6.2(d)], the positive slope of the curves in water rich region indicates $K'_{S,1} > K'_{S,2}$ and the negative slope in non aqueous region indicates $K'_{S,2} > K'_{S,1}$. One then observes preferential solvation of the indicator solute. Thus the presence of ethanol or cyclic ether over water in the water rich region is intelligible in terms of strong self association of water through solvent-solvent hydrogen bonding. As the percentage of non aqueous part increases the self associated structure of water gradually breaks and at an increased mole fraction preferential solvation by water due to solute-solvent hydrogen bonding is observed.

For acetonitrile (1) + water (2) mixtures the slopes of the curve of figure 6.2(b) indicates that the specific interaction part acts differently at least in the four regions of the solvent compositions. Existence of several regions in the vicinity of ions in aqueous-acetonitrile system has also been pointed out by other workers and has been explained in terms of ‘microheterogencity’ of the solvent mixture.
Figure 6.2. Plots of $K_A 4\pi NR^3 3000 \exp(e^2/DRkT)$ versus $x_1$, mole fraction of component(1)
(a) ethanol(1)+ water(2), (b) acetonitrile(1)+ water(2), (c) acetone(1)+ water(2) and (d) 1,4-dioxane(1)+ water(2) mixtures.
For acetone (1) + water (2) mixture [figure 6.2(c)], water has been preferred to acetone in the immediate environment of the ions \( K'_{s,2} > K'_{s,1} \) except in acetone rich region where acetone gets preference over water. While the preference of the solute to water over acetone is easily understood in terms of higher polarity of water, the preference of acetone over water in the acetone rich composition has been explained in terms of free water-acetone interaction through H-bonding.

### 6.2.3 \( \Delta H^0 \) parameter for the ion association

From the analysis of conductance results at different temperatures (288K-308K), \( \Delta H^0 \) values have been calculated from the slope of the plot of \( \log K_a \) vs \( 1/T \) and the results are plotted against \( x_1 \), the mole fraction of solvent (1). \( \Delta H^0 \) values are found to depend systematically on the composition of the mixed solvent (figure 6.3). The exothermic ion pair formation and its systematic variation with the solvent composition indicates that specific solvation effect acts differently in the ion association phenomenon of 1-ethyl-4-cyanopyridinium iodide in mixed aqueous solvents.

### 6.3 Conductance studies in mixed binary non aqueous solvents

#### 6.3.1 Understanding of ion-solvent interaction from Walden product \( A_0 \) and limiting ion conductance values

The limiting molar conductances and \( A_0 \) values of 1-ethyl-4-cyanopyridinium iodide in mixed binary solvents containing ethanol (1) + acetone (2), ethanol(1) + acetonitrile(2) and acetonitrile(1) + acetone(2) have been calculated from experimental results at 293K. The Walden product \( A_0 \) values are found to vary from 59 to 62 in binary mixed solvents and is almost independent of solvent composition. This indicates same type of total solvation of ions through out the entire solvent range. The \( A_0 \) values have been split up into limiting in conductances \( \lambda_i^0 \) using Gill and Cheema method whereby ion conductances in pure organic solvents and in binary mixture of dipolar aprotic solvents can be computed using equation
Figure 6.3 Plots of $\Delta H^0$ versus $x_1$, mole fraction of (a) acetonitrile in acetonitrile+water mixture
(b) I, acetone in acetone+water mixture; II, dioxane in dioxane+water mixture
\[ \lambda^0_{\text{cation}} / \lambda^0_{\text{anion}} = [(5.35 - (0.0103D+\rho_y))/(5.00 - (0.0103D+\rho_y))] \]  
and  
\[ \lambda^0_{\text{cation}} + \lambda^0_{\text{anion}} = \Lambda_0(\text{electrolyte}) \]

where \( \rho_y \) is a parameter equal to 0.85\AA{} for non-associated solvent and 1.13\AA{} for associated solvents. Using \( \lambda^0 \) values for respective ions in pure ethanol, acetone and acetonitrile (1) + acetone(2) mixture, \( r_i \), the average, solvated radii of the ions have been calculated with the help of Gill’s modification of Stokes law:

\[ r_i = |Z| \cdot F^2 / (6 \pi N \lambda^0) + 0.0103D + \rho_y \]

where \( Z \) is the charge of the ions, \( F \) is Faraday’s constant and \( N \) is Avogadro’s number.

In acetonitrile + acetone solvent mixtures the linear dependence of \( r_i \) values on solvent composition indicates similar solvent-solvent interactions. In pure solvents \( r_i \) values are of the order \( r_i \) (ethanol) > \( r_i \) (acetonitrile) > \( r_i \) (acetone). This reflects the extent of solvation of ions in different solvents and hence the preferential solvation of ions is in the order: ethanol>acetonitrile>acetone.

Again the R values which correspond to the average distance between the ions forming contact and solvent separated ion pairs have been analysed using the equation:

\[ R = xa + (1 - x)(a + ms) \]

where \( x \) is the mole fraction of contact ion pairs \( m \) is the number of solvent molecules engaged in the formation of solvent separated ion pairs, \( a \) and \( s \) denote the sum of crystallographic radii of the ions and diameter of the sphere corresponding to average volume per solvent molecule respectively. The results show that specific short range interactions act differently in ethanol, acetonitrile and acetone and are more pronounced in ethanol than in acetonitrile than in acetone.

### 6.3.2 Ion association and solvation effects

Association constant \((K_a)\) values in acetonitrile(1) + acetone(2), ethanol(1) + acetone(2) and ethanol(1) + acetonitrile(2) mixtures have been calculated by using Shedlovsky’s conductance equation at 293K. The results have been analysed using scheme (1). A plot of
L.H.S. of equation (6.4) versus $x_1$ for different solvent systems are shown in Fig.(6.4). It appears from the plot [Fig. 6.4(a)] that for acetonitrile(1) + acetone(2) mixtures a linearity (except in higher mole fraction region of acetonitrile) is obtained. The positive slope indicates that ($K'_{S.1} > K'_{S.2}$). Thus in acetonitrile+acetone mixtures acetonitrile solvent separated ion pair predominates to some extent and the linear variation indicates similar solvation interaction of the component solvent molecules with the solute$^{16}$ over the entire range of solvent compositions. Such observations have also been reported by other workers$^8$.

In ethanol(1) + acetone(2) and ethanol(1) + acetonitrile(2) mixtures the plot passes through a minimum in the mole fraction region $\sim 0.6$ of ethanol [Fig. 6.4(b)]. The deviation is more pronounced when acetonitrile is used as a cosolvent of ethanol. A non linearity of the plot indicates different solvent-solvent interactions in different regions of the solvent system.

The solvation characteristics at the protic rich end of a protic-aprotic mixture may be explained by considering the effect of self-association through solvent-solvent hydrogen bonding$^6$. On the aprotic end individual protic molecules may interact with the individual molecules of the main component with little disruption of its weak dipole-dipole interaction structure and the ions are mostly solvated with the main component.

### 6.4 Conclusion

1-ethyl-4-cyanopyridinium iodide has been found to be a good reporter of solvent interaction. Unlike spectrophotometric studies conductance measurements reflect only the ground state characteristics of the solute and as such will depend very much on specific and non-specific solute-solvent and solvent-solvent interactions.

Results of conductance measurements have been analysed to get $\Lambda_{0\eta}$ and $K_{A}$ values. Variation of Walden product ($\Lambda_{0\eta}$)values in different solvent systems has been explained in terms of specific solvent-solvent and ion-solvent interactions. The association constant ($K_{A}$) values have been separated into electrical and specific short range
Figure 6.4 Plot of $K_A \left[ \frac{4\pi NR^3}{3000} \exp\left(\frac{e^2}{DRkT}\right) \right]$ versus $x_1$ in (a) acetonitrile (1) + acetone (2) mixtures, (b) ethanol (1) + acetone (2), (●) and ethanol (1) + acetonitrile (2) mixtures, (○).
contribution according to scheme(I). The results lead to the conclusion that specific solvation effect is important in the ion association phenomenon of 1-ethyl-4-cyanopyridinium iodide. In mixed binary solvent systems the results are intelligible in terms of microheterogeneity of the binary mixtures. In protic-protic and protic-aprotic solvent mixtures the microheterogeneity arises primarily due to specific solute-solvent and solvent-solvent hydrogen bonding. In aprotic-aprotic solvent systems both specific and nonspecific interactions play significant roles for developing microheterogeneity in the mixture. Thus tendency of ions to associate in pairs depends upon a balance of coulombic, thermal and solvation forces and specific short range solvation effect is important in the ion association phenomenon of 1-alkylpyridinium iodide in the whole range of solvent composition in mixed binary solvent system.
References