Chapter 3: Experimental Procedure

3.1 Solute

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   3.2.2 Physical properties of solvents

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3.1 Solutes

The 1-alkylpyridinium iodides are usually prepared by quaternising the amine with iodomethane or iodoethane\(^1\)\(^2\) in the dark. These compounds are ionic and are extremely soluble in water and alcohol. In the present investigation 1-ethyl-4-cyanopyridinium iodide was chosen as the solute. 4-cyano pyridine (Koch light) was used without further purification. Iodoethane was prepared by the action of iodine and red phosphorous on ethyl alcohol\(^3\).

1-Ethyl-4-cyanopyridinium iodide was prepared by mixing the components in acetone and stirred in the dark for about three days\(^2\). After the reaction was over the excess reactants were removed by washing with ether (sodium dried).

The compound was dried in vacuum. It was then recrystallised from dry ethanol. The process of recrystallisation was done until the crystal gave identical spectra before and after the recrystallisation process. 1-ethyl-4-cyanopyridinium iodide is highly hygroscopic. All the operations were carried out in a desiccated chamber. The purity of the compound was checked by noting the melting point, the longest wave length band maximum, \(\lambda_{\text{max}}\) and the corresponding molar extinction co-efficient value (\(\varepsilon\)) as follows:

1-ethyl-4-cyanopyridinium iodide, found

- \(m.p.=140^\circ C\) (lit. 140 - 141\(^\circ C\))
- \(\lambda_{\text{max}}\) (in \(CH_2Cl_2\)) = 484 nm (lit. 482 nm)
- \(\varepsilon\) (in \(CH_2Cl_2\)) = 1210 \(dm^3\) mol\(^{-1}\) cm\(^{-1}\) (lit 1200 \(dm^3\) mol\(^{-1}\) cm\(^{-1}\))

3.2 Solvents

Solvents used were water, ethanol, acetonitrile, acetone and 1,4-dioxane. All of them were purified and dried by the standard procedures\(^3\).

3.2.1 Solvents Purification

Water for conductance measurement was doubly distilled and degassed. The specific conductance of the water was less than 3\(\times\)10\(^{-6}\) S cm\(^{-1}\).
Ethanol was first dried over lime and then dried by means of magnesium activated with iodine. To a flask provided with a reflux condenser were added 0.5 g iodine, 5 g of magnesium and 50-75 ml of ethanol. The flask was then warmed until the iodine disappeared. If vigorous evolution of hydrogen did not occur, 0.5 g of iodine was added and the mixture heated until all the magnesium was converted to the ethylate. An additional 900 ml of ethanol was then added and the mixture boiled for half an hour under reflux. The product was then distilled with exclusion of moisture in all glass apparatus. The final product was obtained by distillation over molecular sieve 3Å.

Acetonitrile was purified by distilling from phosphorous pentoxide (P₂O₅) in all glass apparatus protected from air by P₂O₅ tube. The distillation procedure was repeated until phosphorous pentoxide in the still pot no longer became coloured. The acetonitrile was then distilled over anhydrous potassium carbonate to remove traces of phosphorous pentoxide and finally it was distilled over molecular sieve 3Å.

Acetone was purified by boiling the commercial product with potassium permanganate and distilled over anhydrous potassium carbonate. The product was then dried over calcium chloride and finally distilled over molecular sieve 3Å.

1,4-Dioxane was boiled under reflux for about seven hours with 10% of its volume of 1N hydrochloric acid, a stream of air being passed through the solution, then distilled. The distillate was treated with potassium hydroxide and aqueous layer removed. It was then allowed to stand over pellets of potassium hydroxide for one day and dried over metallic sodium for several hours. It was then refluxed and distilled. Immediately prior to use all solvents were distilled after refluxing with calcium hydride. This ensured the absence of peroxides or other oxidising agents. Mixed solvents were prepared by carefully mixing the component solvents.
3.2.2 Physical properties of solvents

Physical Properties of the solvents used in the study have been given in the tables 3.1 – 3.5. The densities were measured in a 20 cm$^3$ pyknometer at different temperatures. The dielectric constant of the pure and mixed solvents were interpolated from literature value$^{4-6}$. Some of the densities($\rho$) and viscosities($\eta$) were taken from literature. For viscometric studies of the binary solvent mixture, solvents of different composition were prepared by weight dilution of pure solvents. Kinematic viscosities were measured at the desired temperature (accurate to $\pm 0.01$K) using a suspended UBBELOHDE type viscometer$^{7-8}$ Densities were measured by using Oswald sprengel picnometer having a bulb volume of 20 cm$^3$. The over all accuracy of the viscosity was estimated as $\pm 0.1$%. All measurements were done in a water thermostat having an accuracy of 0.01K.

3.3 Measurement of conductance data

Precision conductivity bridge (Systronics-304) capable of measuring Conductance at 1000Hz, with a calibrated digital conductivity meter with an accuracy of $\pm 0.2\%$ in the range of 2 $\mu$S to 2S and a dip type immersion conductivity cell were used for the measurement of electrolytic conductivities. The measurements are made over the temperature range 288K–308K ($\pm 0.2$K). The cell compartment consisted of a glass vessel fitted with a standard joint glass stopper to which, the dip type immersion conductivity cell was introduced. The vessel was kept in a water thermostat where temperature was controlled to within ($\pm 0.2$K). The instrument was standardised with KCl solution of known concentration equilibrated at the same temperature. The reproducibility of the results was ensured by performing several independent replicate experiments. The molar conductivities corrected for the conductivity of the solvents of about eight solutions in the concentration range of $10^{-3}$ to $10^{-4}$ mol dm$^{-3}$ of 1-ethyl-4-cyanopyridinium iodide for a given solvent composition were examined at different temperatures. All solutions were prepared by proper dilution of a stock solution of weighed sample of 1-ethyl-4-cyanopyridinium iodide in a given solvent mixture.
Table 3.1 Density ($\rho$)\textsuperscript{5} Dielectric constant ($D$)\textsuperscript{4} and Viscosity($\eta$)\textsuperscript{5} for ethanol + water mixtures at 293-308K

<table>
<thead>
<tr>
<th>Mole fraction of ethanol</th>
<th>293K $\rho$/g cm\textsuperscript{-3}</th>
<th>293K $D$</th>
<th>293K $\eta$/(cP)</th>
<th>298K $\rho$/g cm\textsuperscript{-3}</th>
<th>298K $D$</th>
<th>298K $\eta$/(cP)</th>
<th>303K $\rho$/g cm\textsuperscript{-3}</th>
<th>303K $D$</th>
<th>303K $\eta$/(cP)</th>
<th>308K $\rho$/g cm\textsuperscript{-3}</th>
<th>308K $D$</th>
<th>308K $\eta$/(cP)</th>
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</thead>
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<tr>
<td>0.0000</td>
<td>0.9982</td>
<td>80.36</td>
<td>1.005</td>
<td>0.9976</td>
<td>78.540</td>
<td>0.8937</td>
<td>0.9950</td>
<td>76.65</td>
<td>0.8007</td>
<td>0.9940</td>
<td>75.000</td>
<td>0.7225</td>
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<tr>
<td>0.0890</td>
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<td>2.183</td>
<td>0.9644</td>
<td>76.090</td>
<td>1.8150</td>
<td>0.9640</td>
<td>65.68</td>
<td>1.5530</td>
<td>0.9615</td>
<td>63.660</td>
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<tr>
<td>0.2810</td>
<td>0.9138</td>
<td>50.39</td>
<td>2.870</td>
<td>0.9098</td>
<td>49.110</td>
<td>2.4000</td>
<td>0.9057</td>
<td>47.84</td>
<td>2.0200</td>
<td>0.9015</td>
<td>46.570</td>
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<td>0.8591</td>
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<td>0.8160</td>
<td>35.945</td>
<td>1.5290</td>
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<td>0.8125</td>
<td>28.200</td>
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<td>1.2790</td>
<td>0.8045</td>
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<td>1.1470</td>
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<td>0.9140</td>
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</table>
Table 3.2 Density ($\rho$) and Dielectric constant ($D$) and Viscosity($\eta$) for acetonitrile + water mixture at 288-303K

<table>
<thead>
<tr>
<th>Mole fraction of acetonitrile</th>
<th>288K</th>
<th>293K</th>
<th>298K</th>
<th>303K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_l$</td>
<td>$\rho$ / g cm$^{-3}$</td>
<td>$D$</td>
<td>$\eta$ / (cP)</td>
<td>$\rho$ / g cm$^{-3}$</td>
</tr>
<tr>
<td>0.000</td>
<td>0.9991</td>
<td>82.22</td>
<td>1.1404</td>
<td>0.9982</td>
</tr>
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<td>0.9832</td>
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<td>1.1600</td>
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<td>0.300</td>
<td>0.8980</td>
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<td>0.9300</td>
<td>0.8938</td>
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<tr>
<td>0.500</td>
<td>0.8527</td>
<td>48.80</td>
<td>0.6500</td>
<td>0.8482</td>
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<tr>
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<td>0.8094</td>
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<td>0.4300</td>
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<tr>
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<td>37.30</td>
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<td>0.7820</td>
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Table 3.3. Density ($\rho$) Dielectric constant ($D$) and Viscosity($\eta$) for acetone + water Mixture at 293-308K

<table>
<thead>
<tr>
<th>Mole fraction of acetone $x_1$</th>
<th>$\rho / \text{g cm}^3$</th>
<th>$D$</th>
<th>$\eta / (\text{cP})$</th>
<th>$\rho / \text{g cm}^3$</th>
<th>$D$</th>
<th>$\eta / (\text{cP})$</th>
<th>$\rho / \text{g cm}^3$</th>
<th>$D$</th>
<th>$\eta / (\text{cP})$</th>
<th>$\rho / \text{g cm}^3$</th>
<th>$D$</th>
<th>$\eta / (\text{cP})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>0.9982</td>
<td>80.36</td>
<td>1.005</td>
<td>0.9976</td>
<td>78.54</td>
<td>0.8937</td>
<td>0.9956</td>
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<td>0.9606</td>
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<td>1.723</td>
<td>0.9478</td>
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<td>1.3855</td>
<td>0.9375</td>
<td>58.00</td>
<td>1.1155</td>
<td>0.9330</td>
<td>56.00</td>
<td>0.9550</td>
</tr>
<tr>
<td>0.2678</td>
<td>0.9240</td>
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<td>0.9113</td>
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<td>1.1404</td>
<td>0.9012</td>
<td>46.50</td>
<td>0.9660</td>
<td>0.8930</td>
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</tr>
<tr>
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<td>0.8523</td>
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<td>0.6970</td>
<td>0.8343</td>
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<td>0.6240</td>
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<td>32.20</td>
<td>0.5250</td>
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<td>0.6870</td>
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<tr>
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<td>0.8144</td>
<td>24.50</td>
<td>0.405</td>
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<td>0.3890</td>
<td>0.7932</td>
<td>23.00</td>
<td>0.3740</td>
<td>0.7900</td>
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<td>0.8002</td>
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<td>0.3550</td>
<td>0.7906</td>
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<td>0.3390</td>
<td>0.7850</td>
<td>21.00</td>
<td>0.3310</td>
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<td>0.9375</td>
<td>0.7946</td>
<td>21.60</td>
<td>0.356</td>
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<td>0.7875</td>
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<td>0.7721</td>
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<td>0.7768</td>
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<td>19.86</td>
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</table>
Table 3.4 Density ($\rho$) Dielectric constant ($D$) and Viscosity($\eta$) for 1,4-dioxane + water mixture at 293-308K

<table>
<thead>
<tr>
<th>Mole fraction of 1,4-dioxane ($x_I$)</th>
<th>293K</th>
<th></th>
<th>298K</th>
<th></th>
<th>303K</th>
<th></th>
<th>308K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\rho$ / g cm$^{-3}$</td>
<td>$D$</td>
<td>$\eta$ / cP</td>
<td>$\rho$ / g cm$^{-3}$</td>
<td>$D$</td>
<td>$\eta$ / cP</td>
<td>$\rho$ / g cm$^{-3}$</td>
</tr>
<tr>
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<td>1.005</td>
<td>0.9976</td>
<td>78.54</td>
<td>0.8937</td>
<td>0.99560</td>
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<td>19.07</td>
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<td>1.03060</td>
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<td>1.02940</td>
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### Table 3.5 Density ($\rho$) Dielectric constant ($D$) and Viscosity ($\eta$) of mixed binary non aqueous solvents for different mole fraction ($x$) at 293K

<table>
<thead>
<tr>
<th>Solvent mixtures</th>
<th>$x_1$</th>
<th>$\rho$ g/cc</th>
<th>$D$</th>
<th>$\eta$/cP</th>
<th>$x_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile(1)+acetone(2)</td>
<td>0.0000</td>
<td>0.7920</td>
<td>21.07</td>
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<td>1.0000</td>
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<tr>
<td></td>
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<td>Ethanol(1)+acetone(2)</td>
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<td>1.0000</td>
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<td></td>
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<td>0.329</td>
<td>0.0000</td>
</tr>
<tr>
<td>Ethanol(1)+acetonitrile(2)</td>
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<td>0.7857</td>
<td>25.07</td>
<td>1.200</td>
<td>1.0000</td>
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<tr>
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<td>0.1828</td>
</tr>
<tr>
<td></td>
<td>1.0000</td>
<td>0.7827</td>
<td>36.80</td>
<td>0.357</td>
<td>0.0000</td>
</tr>
</tbody>
</table>
3.3.1 Determination of ion association constant

There are three problems in the determination of ion association constant, relating to the ion association phenomena viz., to determine the nature of species present, to evaluate the concentration quotient and to determine the activity quotient. The recent results show that in a solution of low dielectric constant an electrolyte exists mainly as contact ion pair ($A^- B^+$), solvent separated/shared ion pair ($A^+ \parallel B^-$) and free ions. Higher ionic aggregates are important only in concentrated solutions and they were assumed to be absent in dilute solutions used. The activity co-efficients have to be taken in to consideration specially for ionic species present in the solution. The ion pair species should have some activity co-efficient but this is non-determinable at present. The usual practice is to assume it to be unity.

3.3.2 Method of analysis of data

Considering the precision of the conductance data (ca. ± 0.2%) the association constants were calculated from the conductance data by Fuoss and Kraus method and Shedlovsky method. Equation (3.1) is used in the Fuoss and Kraus method.

\[
F(z)/A = K_{A}^{\sqrt{2}} A_0^2 \left[ c A f_c^2 / F(z) \right] + 1 / A_0
\]

\(A\) is the molar conductance at a concentration \(c\) in mol dm\(^{-3}\), \(A_0\) is the limiting molar conductance. \(K_{A}\) is the observed association constant.

\[
F = 4/3 \cos^2{1/3 \cos^{-1}{(-3^{2/3} z/2)}}
\]

\(z = [S / A_0^{2/3} (c A)^{1/2}; S = \alpha \Lambda_0 + \beta_0\)

\(\beta_0 = 82.501 \eta (D T)^{1/2}, \eta\) is the dielectric constant, \(T\) is the temperature in Kelvin, \(\eta\) is the viscosity (cP), \(\alpha_0 = 0.8204 \times 10^6 (D T)^{3/2}\). The degree of dissociation is related to \(F\) by the equation.

\[
y = A / (A_0 F)
\]

\(f_c\) is the mean activity co-efficient of the free ions and is calculated using the equation

\[
-\log f_c = A / [1 + B R (D T)^{1/2}]
\]

where \(A = 1.8247 \times 10^6 (D T)^{3/2}\) and \(B = 0.5029 \times 10^{16} (D T)^{1/2}\)
I is the ionic strength of the solution and R is the maximum centre to centre distance between the ions in the ion pair. There exists at present no method of determining the value of R uniquely\(^{13}\), according to Justice\(^{14,15}\) R should be numerically identified with Bjerrum radius\(^{16}\) \((q)\) which for the uni-univalent electrolyte is given by the expression, 
\[ q = e^2/2DkT, \]
where \(e\) is the electronic charge and \(k\) is the Boltzmann’s constant\(^{16}\). Here the \(q\) value depends on the dielectric constant only. Hawlicka\(^{17}\) has shown that Bjerrum distance \(q\) does not fit the experimental data in acetonitrile + water mixture. The curve fitting methods with conductance equations based on the primitive model shows the existence of wide range of \((R, K_t)\) pairs giving almost good fits to the experimental data\(^{18,19}\). Because of this problem the analysis of data for such systems has presented some difficulty. In order to treat the data in our system the \(R\) value is assumed to be equal to \((a+d)\), where \(a\) is sum of crystallographic radii of the ions and is approximately equal to \(5\ \text{Å}\) and \(d\) is an average distance corresponding to the side of a cell occupied by a solvent molecule and is given by\(^{6}\), 
\[ d = 1.183(M/\rho)^{1/3} \text{Å} \]
where \(M\) is molecular weight of the solvent and \(\rho\) is the density of solution. For mixed solvents \(M\) is replaced by mole fraction average molecular weight.

\[ M_{av} = (x_1M_1 + x_2M_2) = M_1M_2/(w_2M_1 + w_1M_2) \]  \hspace{1cm} \text{...(3.6)}

where \(x_1\) and \(w_1\) are the mole fraction and weight fraction of component 1 of molecular weight \(M_1\) and \(x_2\) and \(w_2\) are the mole fraction and weight fraction of component 2 of molecular weight \(M_2\). The variation of the distance parameter does not significantly alter the \(A_0\) value as it has been reported previously\(^{9,17}\). This means that the \(A_0\) is independent to the assumed model. The association constant \(K_A\), however, depends on \(R\) in two ways. \(R\) affects strongly the degree of association and influences also the activity co-efficient of free ions. It has been found for a solution of weak ionic association \((K_A \approx 100)\) that the difference between the different models is negligible\(^{20}\). For other solution \(K_A\) value are calculated on the basis of relation \((R = a + d)\). For strongly associated ionic solution where \(K_A\) values lie in the range \(1 \leq K_A \leq 10^5\) the extrapolation by means of Shedlovsky’s\(^{12}\) equation is recommended. In Shedlovsky method the following equation is used

\[ 1/AS(z) = (K_A/A_0^2)\{c + Mf_0^2S(z)\} + 1/A_0 \]  \hspace{1cm} \text{...(3.7)}
\( A \) is the molar conductance at a concentration \( c \) in mol dm\(^{-1}\), \( A_0 \) is the limiting molar conductance and \( K_1 \) is the observed association constant the other symbols are given by

\[
S(z) = \frac{\sqrt{z}}{2} + \frac{(1+(\sqrt{z}/2)^2)^{1/2}}{2} \ldots (3.8)
\]

\[
z = \frac{(a_0 A_0 + \beta_0)}{(A_0)^{1/2} (cA_0^{1/2})} \ldots (3.9)
\]

\[
\beta_0 = 82.501/\eta (DT)^{1/2}, D \text{ is the dielectric constant of medium } \eta \text{ is the viscosity (cP) and } a_0 = 0.8204 \times 10^6 (DT)^{1/2}. \text{The degree of dissociation } \gamma \text{ is related to } S(z) \text{ by the equation}
\]

\[
\gamma = \frac{AS(z)}{A_0} \ldots (3.10)
\]

\( f_+ \) is the mean activity coefficient of the free ions and is calculated using equation (3.5).

The method is iterative. A preliminary value of \( A_0 \) is obtained by extrapolating the experimental plot as \( 1/A \) vs \( Ac \) as a first approximation. Calculations are carried out using above equations iteratively by the method of least squares till the error of estimation was 0.01\%. A computer program was written, for which the input is the data set \((A; c), R, D, \eta \text{ and } T \) and equations (3.5, 3.7-3.10). All the calculations were carried out using computer program on IBM PC-AT/386.

It is now well established that in a solution of low dielectric constant an electrolyte exists as the following distinctly different species\(^9\text{,}21\). These are (1) the contact ion pairs (CIP) where the two oppositely charged ions are in physical contact, (2) the solvent shared/ separated ion pairs (SSIP) the two ions forming an ion pair remain separated by one or more solvent molecules and (3) the free ions. Interionic attraction coupled with the thermal motion lead to the following equilibrium in a pure solvent.

\[
K_R K_S
A^+ B^- \leftrightarrow (A^+ B^-) \leftrightarrow A^+ B^-
\ldots (2.14)
\]

and the conductometrically determined association constant \( K_1 \) is given by

\[
K_1 = \frac{[A^+ B^-] + [A^+ B^-]}{[A^+ B^-]^{1/2} f_+^2} = K_R(1+K_S)
\ldots (2.18)
\]

The distribution between the different species is determined by the equilibrium constants \( K_S \) and \( K_R \) and a complete solution of this problem is to determine the nature of SSIP and to measure the position of each equilibrium. Measurements in a pure solvent can not provide \( K_R \) and \( K_S \) separately. But the resolution can be achieved by using a mixed binary solvents. To this end we propose the following scheme (I) representing various
equilibria (including the solvent molecules explicitly). In a mixed binary solvent we may write

\[
\begin{align*}
\text{Si}^+ \text{A}^+ + \text{B}^- & 
\xrightarrow{K_R} \quad (\text{free ions}) \\
\text{K}_{AC} & \quad \text{K}_{Si} \\
(A^+, B^-) + \text{Si} & 
\xrightarrow{K'}_{Si} \\
& (i\text{-th solvent separated ion}) \\
& (contact ion pairs)
\end{align*}
\]

**Scheme 1**

\(K_{AC}\) represents the formation of contact ion pair species from the solvated ions and is expressed by equation (2.8) as \(K_{AC} = K_R K_S\). The conductometrically determined association constant, \(K_A\), is then given by

\[
K_A = K_{AC}(1 + |\text{Si}|/K_{Si}) \quad (i = 1, 2) \quad \ldots (3.11)
\]

\[
K_A = K_{AC}(1 + K'_{Si}, |\text{Si}|) \quad \ldots (3.12)
\]

When more than one solvent is engaged in the formation of solvent separated ion pairs the equation (3.12) becomes

\[
K_A = K_{AC}(1 + K'_{S,1} |\text{Si}| + K'_{S,2} |\text{Si}|) \quad \ldots (3.13)
\]

Replacing solvent activities by mole fractions and noting that for dilute solution of electrolyte \(x\) may be replaced by \((1-x)\), we have

\[
K_A = K_{AC}(1 + K'_{S,2} + (K'_{S,1} - K'_{S,2})x_1) \quad \ldots (3.14)
\]

The parameter \(K_{AC} \cdot K_R \cdot K_S\) denotes the formation of a contact ion pair species from the solvated ions and can be factored into an electrostatic contribution \((K_{el})\) and specific short-range interactions \((K_{SP})\). \(K_{el}\) is given by the Fuoss equations and the equation (3.14) may be written as

\[
K_A = [(4 \pi N R^2/3000) \exp(e^2/DRkT)]/K_{SP}(1 + K'_{S,2} + (K'_{S,1} - K'_{S,2})x_1) \quad \ldots (3.15)
\]
The exponential part depends on $D$, the dielectric constant of mixed binary solvent and is dependent on the mole fraction $x_1$. Dividing $K_A$ by the electrostatic contribution one gets:

$$K_A/[(4\pi NR^3/3000)\exp(e^2/4DRkT)] = [K_{SP}(1+K'_{S,2}) + (K'_{S,1} - K'_{S,2})x_1] \quad \ldots(3.16)$$

A plot of the L.H.S. of equation (3.16) versus $x_1$ at a particular temperature would give a curve, the slopes of which at different parts give an idea of specific solvation effect.
References