CHAPTER II

EXPERIMENTAL METHODS
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The methods utilised in the experimental work presented in this dissertation are

1) pH - metric measurements
2) Spectrophotometric measurements
3) Solubility measurements

A brief account of the methods are given here.

1) pH - metric measurements

\[ \text{pH - metric measurements of hydrogen ion concentration in mixed solvents, calibration of Glass - electrode} \]

Most of our works are related to the determination of dissociation constants of the acids of different charge type like

\[ \text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \quad \text{(ionic)} \]
\[ \text{LH}^+ \rightleftharpoons \text{L}^- + \text{H}^+ \quad \text{(isoelectric)} \]
\[ \text{RH}_2^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{RH}^+ \quad \text{(Zwitterion ionic type)} \]

in aqueous and mixed solvents.

The \( \text{H}^+ \) ion concentrations (rather activity) in aqueous solutions are usually measured with the help of \( \text{pH} \)-meter. A Systronics Digital \( \text{pH} \)-meter (± 0.01 pH units) with a combined glass and calomel electrode maintained at 298\( ^\circ \)K and also a Knick,
Labor pH-meter, Elektronische Meßgeräte, Berlin maintained at the same temperature were used for pH-measurements.

But the measurements of $H^+$ ion concentrations in mixed or non-aqueous solvents present a difficult problem. The measurement of $H^+$ ion using hydrogen electrode suffers from the following limitations:

i) The e.m.f. of hydrogen electrode is taken to be zero in all solvents and at all temperatures.

ii) Experimental methods have been difficult and measurements utilising the hydrogen electrode can be applied only to systems where complicating reduction reactions are absent.

The measurements of $H^+$ ion concentrations using glass electrode suffer from the following limitations:

i) Glass-electrode potentials change in going from aqueous to mixed solvents.

ii) Liquid junction potentials of uncertain magnitude may vitiate the results appreciably. The liquid junction potential increases with the increase in the percentage of organic solvents. This is the most serious drawback in measuring the $H^+$ ion concentration in mixed solvents.
iii) Trouble arises due to decreased solubility of the electrolytes in mixed solvents particularly when the organic solvent content is high.

iv) Sensitivity of the glass electrode decreases with the increase in organic solvent due to increase in resistance.

v) Considerable difficulty arises due to lack of suitable buffers to be used as standards in different mixed solvents.

The determination of $H^+$ ion concentrations has attracted attention of workers like Bates, Robinson and co-workers 6-8 and de Ligny and co-workers. 9-11

Van Uitert and Hass 1-2, however, measured the hydrogen ion concentrations in mixed solvents pH metrically in a simple way.

In order to overcome the effects due to the change in glass-electrode potentials and the liquid-junction potentials of uncertain magnitude, the glass-electrode was calibrated in different mixed solvents in the following way.

The meter readings in mixed solvents are referred to as $B$ values. To calibrate the glass electrode, $10^{-4}$ (M) HCl solutions in mixed solvents were measured against $10^{-4}$ (M) HCl in aqueous solution. The correction factor $\log (\frac{U_H}{\mathcal{E}})$ was calculated from the relationship.

(65)
\[ -\log [H^+] = B + \log [U_B] \]

Where \([H^+]\) is the stoichiometric hydrogen ion concentration in the aqueous and in mixed solvents.

The method has been extensively utilised by Gentile et al.\textsuperscript{12}. Irving and Manhot\textsuperscript{13} measured the pH-meter correction in dioxane-water assuming complete dissociation of \(HCl\) in dioxane-water mixtures. But \(HCl\) is known to be associated to a large extent in solutions having 70% and 82% by weight of dioxane. It is likely that it would behave as weak acid in other organic solvents when the dielectric constant is low.

Pal, Bhattacharyya, Lahiri and Aditya,\textsuperscript{3-5} therefore, preferred \(10^{-4} (M)\) \(HClO_4\) solutions as standard instead of \(10^{-4} (M)\) \(HCl\). Since \(ClO_4^-\) anion is large, it may be assumed to have less chance to be solvated and associated. \(LiClO_4\) is actually known to be dissociated in dioxane. The measurements of the strengths of the acids in acetic acid medium showed that \(HClO_4\) is much stronger than other acids. Yet the possibility of association of \(HClO_4\) in high percentages of organic solvents (90% by weight or above) can not be ruled out. To verify the accuracy of their results, Lahiri, Aditya and Co-workers\textsuperscript{3-5} measured the \(H^+\) ion concentrations based on \(10^{-4} M\) \(HClO_4\) and compared the results with the theoretical values calculated from Harned's data\textsuperscript{14} (formic acid and formate buffer). The results agreed well upto 70%.
dioxane. The discrepancy, however, is large in 82% dioxane. Redetermined values of Danyluk, Taniguchi and Jans reduce the difference considerably. Their results agreed well with the values reported by Irving and Manhot.

In the works described in this dissertation, $\text{H}^+$ ion concentrations were always measured taking $10^{-4} \text{ M HClO}_4$ as standard. The pH meter was first standardised with potassium hydrogen phthalate (M/20) buffer and then with $10^{-4} \text{ M HClO}_4$ in water. The glass-electrode was then kept immersed in the appropriate solvent medium for equilibration and the meter reading of $10^{-4} \text{ M HClO}_4$ in the particular solvent medium was taken for further standardisation. The method gives reproducible results. The glass-electrode was calibrated before each set of measurement to avoid any error creeping into the result due to the change in sensitivity of the glass electrode.

It has been noted that the glass-electrode loses its sensitivity after several months. However, the life of the electrode is little prolonged and the sensitivity may be restored if after each set of measurement, the glass-electrode is dipped in concentrated solution of HCl for about ten minutes and then stored in distilled water. However, occasional replacement of the glass-electrode is necessary.
Glass electrodes have been extensively utilised by Hepler, Woolley and Co-workers\textsuperscript{15-18} in the determination of pH values of water and $pK_a$ values in different aquo-organic mixtures.

2) \textbf{SPECTROPHOTOMETRIC MEASUREMENTS} \textsuperscript{19-21}

The ligands used in the present investigation are 2, 2' - bipyridyl and 1, 10 - phenanthroline. They absorb strongly in the U.V. region. The positions of the absorption maxima change with the pH of the solutions. The absorption curves of the ligands in ionic and molecular forms were obtained by measuring the U.V. spectra of the ligands in excess acid (HClO\textsubscript{4}) and in excess alkali (NaOH) solution. The absorption maxima for the ionic and molecular forms were found to be 301 nm and 280 nm (for 2, 2' - bipyridyl) and 272 nm and 264 nm (for 1,10-phenanthroline). The absorption maxima were very slightly affected in different organic solvents.

Any wavelength other than isosbestic point can be utilised to calculate the dissociation constant of the ligands, but to obtain accurate values, measurements were taken at the analytical wavelengths (which are 300 and 305 nms for 2,2'-bipyridylyl, 255 and 260 nms for 1,10 - phenanthroline). At these wavelengths, there are maximum difference in density between
the species.

For the determination of the pK-values of ligands in mixed solvents, the optical density readings of the ligand in excess acid (0.01 N - 1N HClO₄ or more HClO₄ in higher percentages of organic solvents such as Ethylene Glycol, Dioxane etc. as the situation demands) and in alkali (0.1 N NaOH) and at intermediate pH's (depending on the pK-values of the ligands) were taken at the respective analytical wavelengths. The blank solutions were of the same composition as in the experimental solutions except the ligands. The thermodynamic dissociation constant $K_T$ for the equilibrium $LH^+ \rightleftharpoons L + H^+$ ($L = 2,2'$-bipyridyl, 1,10-phenanthroline) can be represented by

$$K_T = \frac{a_L \times a_{H^+}}{a_{LH^+}} = \frac{C_L \times C_{H^+}}{C_{LH^+}} \times \frac{f_L \times f_{H^+}}{f_{LH^+}}$$

$$\approx \frac{C_L \times C_{H^+}}{C_{LH^+}}$$

(in very dilute solutions and since $f_{H^+} = f_{LH^+}$)

Thus, $pK_T = pH + \log \frac{C_{LH^+}}{C_L}$

$$= pH + \log \frac{c_{-} - c_{M}}{c_{1} - c}$$

where $c_{1}$, $c_{M}$ and $c$ represent the extinction co-efficients of the ion, molecule and mixtures of the ion and molecule at the analytical wavelength $\lambda$. 

(69)
The degree of ionization of $LE^+$ changes with pH and as a consequence, $\varepsilon$ changes with the change in pH. This $\varepsilon$ is determined for different degree of neutralisation corresponding to different pH's and a number of values of p$K$ are obtained to get an average p$K$.

In actual practice, the solutions having the same concentration of the substance are taken and the optical density of the solutions at pH's corresponding to the condition that the whole of the substance exists in molecular form and ionic form and some intermediate pH's when both molecular and ionic forms exist, are taken using the same cells. Under these conditions,

$$ pK_T = pH + \log \frac{d - d_M}{d_1 - d} $$

$d_M$, $d_1$ and $d$ are the optical densities of the molecular and ionic forms and at intermediate pH's respectively. 

So from measurements of $d_M$, $d_1$ and $d$ at different pH's at the analytical wavelengths, the p$K$ values can be calculated. The measurements were made with a Varian Techtron (Series 634) Spectro-photometer maintained at 298°K.
3) **SOLUBILITY MEASUREMENTS**

For the solubility measurements at a definite temperature in mixed solvents, saturated solutions containing excess of the compounds were prepared in the appropriate solvent composition. These solutions were taken in Campbell solubility apparatus fitted with sintered disc and fine tube. The solutions were allowed to equilibrate in a thermostat (Remi Ultra Cryostat: C 700) maintained at definite temperature (± 0.01) for 24 hours. After equilibration, the solution was filtered by inverting the apparatus in the thermostat. A definite amount of the solution was taken and diluted with appropriate solvent, if necessary and analysed titrimetrically, pH metrically and spectrophotometrically depending on the nature of the experiments. The error involved in the solubility measurements would be about 0.2% - 0.5%.
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