SUMMARY

Ethylacetate as a polar solvent

It is probable that the solvent may ionise in any of the following ways:

\[ \text{CH}_3\text{COOC}_2\text{H}_5 \rightleftharpoons \text{CH}_3\text{CO}^+ + \text{OC}_2\text{H}_5^- \quad \ldots \ldots \quad (i) \]

\[ \text{CH}_3\text{COOC}_2\text{H}_5 \rightleftharpoons \text{C}_2\text{H}_5^- + \text{CH}_3\text{COO}^- \quad \ldots \ldots \quad (ii) \]

\[ 2\text{CH}_3\text{COOC}_2\text{H}_5 \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5.H^+ + \text{CH}_2\text{COOC}_2\text{H}_5^- \quad \ldots \ldots \quad (iii) \]

The mode of ionisation as represented by equation (ii) has been ruled out and is supported by the work of Booth and Martin.

Ethylacetate has been studied as a polar solvent with a view to study its nature. Solubilities of a large number of chlorides and other compounds have been determined quantitatively and qualitatively. Ethylacetate forms solvates with a large number of compounds including Lewis acids and organic tertiary bases. The solvate formation has been indicated by the actual isolation of solvates, conductivity measurements of the solutions of different compounds in ethylacetate. The solutions of Lewis acids and organic tertiary bases have been found to be fairly conducting which suggests the formation of ion pairs. Various modes of ionisation of these complexes have been discussed and it is suggested that the solvates of Lewis acids ionise as:

\[ \text{MCl}_3 \cdot \text{CH}_3\text{COOC}_2\text{H}_5 \rightleftharpoons \text{CH}_3\text{CO}^+ + \left\{ \text{MCl}_3(\text{OC}_2\text{H}_5) \right\}^- \]
where $M$ and $M'$ represent the trivalent and tetravalent metals.

The hypothetical solvates of bases may ionise in either of the two modes as:

$$
\begin{align*}
    & \text{B.CH}_3\text{COOC}_2\text{H}_5 \rightarrow \text{BCH}_3\text{CO}^+ + \text{OC}_2\text{H}_5^- \\
    & \text{B.CH}_3\text{COOC}_2\text{H}_5 \rightarrow \text{BH}^+ + (\text{CH}_2\text{COOC}_2\text{H}_5)^-
\end{align*}
$$

Solvolysis of a number of metal halides which are Lewis acids has been carried out in ethylacetate and a number of halide ethoxides have been isolated. The partially solvolysed products (halide ethoxides) also form solvates with ethylacetate. The mechanism of these solvolytic reactions is explained on the basis of the formation of solvates which when refluxed for sufficiently long time, rearrange themselves and produce acetyl chloride and halide ethoxides as:

$$
\begin{align*}
    & \text{MC}1_3 + \text{CH}_3\text{COOC}_2\text{H}_5 \rightarrow \text{MC}1_3\cdot\text{CH}_3\text{COOC}_2\text{H}_5 \\
    & \text{MC}1_3\cdot\text{CH}_3\text{COOC}_2\text{H}_5 \rightarrow \text{CH}_3\text{CO}^+ + \text{MC}1_3(\text{OC}_2\text{H}_5)^- \\
    & \text{CH}_3\text{CO}^+ + \text{MC}1_3(\text{OC}_2\text{H}_5)^- \xrightarrow{\text{refluxing}} \text{CH}_3\text{COCI} + \text{MC}1_2(\text{OC}_2\text{H}_5)
\end{align*}
$$

which may again form a solvate with the excess of the solvent as

$$
\text{MC}1_3(\text{OC}_2\text{H}_5) + \text{CH}_3\text{COOC}_2\text{H}_5 \rightarrow \text{MC}1_3(\text{OC}_2\text{H}_5)\cdot\text{CH}_3\text{COOC}_2\text{H}_5
$$

In the case of tetravalent metals, two chlorine atoms are replaced by ethoxy groups.
The formation of the acid-base complexes between Lewis acids and organic tertiary bases have been studied conductometrically and with the help of visual indicators. A few of the normal salts of the acid base complexes have been isolated and characterised by analysis. All the aforementioned properties have been studied to prove its autoionisation as:

\[
\text{CH}_3\text{COC}_2\text{H}_5 \rightleftharpoons \text{CH}_3\text{CO}^+ + \text{OC}_2\text{H}_5^-
\]

Besides the Lewis acids, protonic acids have also been found to form solvates with ethylacetate and the solutions are very conducting. The ions responsible for the high conductivity of the solutions may be represented as:

\[
\text{HX} + \text{CH}_3\text{COC}_2\text{H}_5 \rightarrow \text{HX.CH}_3\text{COC}_2\text{H}_5 \rightarrow \text{CH}_3\text{COC}_2\text{H}_5\text{H}^+ + \text{X}^-
\]

The high conductivity of the solution suggests the presence of similar ions already in the solvent due to its autoionisation as:

\[
2\text{CH}_3\text{COC}_2\text{H}_5 \rightarrow (\text{CH}_3\text{COC}_2\text{H}_5\text{H})^+ + (\text{CH}_3\text{COC}_2\text{H}_5)^-
\]

From the measurements of the conductivities of the solutions of protonic acids, their strength has been compared and they can be arranged in the order of their descending strength as \(\text{H}_3\text{O}_3\text{F} > \text{H}_3\text{O}_3\text{Cl} > \).
H₂SO₄ > H₂S₂O₇ > CCl₃COOH > CH₂ClCOOH > CH₃COOH. The differentiating effect of ethylacetate on the strength of various organic bases has also been explored. From the measurement of the conductivities of their solutions, from the potential jumps near the neutralisation points in potentiometric titrations and from the shades of the indicators in concentrated and weak solutions, the bases can be arranged in the order of their descending strength as isoquinoline > quinoline > pyridine > α-picoline > piperidine > dimethylaniline > triethylamine > diethylaniline > n-butylamine.

Acid-base neutralisation reactions between protonic acids and various organic bases have been studied, conductometrically, potentiometrically and with the help of various indicator dyes. It suggests a convenient method for the estimation of various nitrogen bases which otherwise are insoluble in water. Methyl orange, crystal violet, dimethyl yellow, thymol blue, methyl red and neutral red have been studied as reversible indicators in ethylacetate. Because of the basic nature of ethylacetate, weak acids like benzoic acid, acetic acid, monochloroacetic acid etc. have been estimated conveniently.