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Ethyl formate and ethyl chloroformate have been used as polar media for a wide variety of chemical reactions.

Solubilities of a large number of organic and inorganic compounds have been quantitatively determined and the two esters have been found to be efficient solvents for the covalent compounds whereas the solubility of electrovalent compounds is very poor due to the low dielectric constants of the solvents.

Solvates of Lewis acids with ethyl formate have been isolated and they have been found to be fairly ionic in nature. As the strong Lewis acids cause immediate decarboxylation of ethyl chloroformate it has not been possible to isolate the corresponding solvates.

No addition compounds of protonic acids and nitrogen organic bases with ethyl formate could be isolated. The protonic acids simply cause decomposition of ethyl chloroformate whereas the nitrogen organic bases do form solvates which have been isolated and characterised.

Conductance measurements of solutions of protonic acids and nitrogen organic bases in ethyl formate have indicated the formation of the corresponding addition compounds which are fairly ionic. The higher conductance of the
solutions of protonic acids in ethyl formate has been explained as due to the existence of the following ionic equilibria:

\[
\text{HCOOC}_2\text{H}_5 + \text{HX} \rightarrow \text{HCOOC}_2\text{H}_5\cdot \text{HX} \rightleftharpoons (\text{H}_n\text{HCOOC}_2\text{H}_5)^+ \cdot \text{X}^-
\]

whereas the conductance of solutions of nitrogen organic bases has been explained as due to the protonation of the base as:

\[
\text{HCOOC}_2\text{H}_5 + \text{B(base)} \rightarrow \text{HCOOC}_2\text{H}_5\cdot \text{B} \rightleftharpoons \text{BH}^+ \cdot \text{HCOOC}_2\text{H}_5^-
\]

The equivalent conductance at infinite dilution \((\lambda_0)\) of the solutions of protonic acids, fluorosulphuric, disulphuric sulphuric, hydrobromic and hydrochloric acids in ethyl formate have been determined and on the basis of these values they have been arranged in the order of decreasing strength as:

\[
\text{FSO}_3\text{H} > \text{H}_2\text{S}_2\text{O}_7 > \text{H}_2\text{SO}_4 > \text{HBr} > \text{HCl}
\]

On the basis of similar determinations, the bases have been placed in the following order of decreasing strength:

Piperidine > α-picoline > quinoline > diethylaniline

Since the protonic acids cause decomposition of ethyl chloroformate, the conductance measurements of their solutions have not been carried out. However, only the nitrogen bases dimethyl and diethyl aniline have been found to be freely miscible with ethyl chloroformate and the higher conductance
of their solutions has been explained as due to the existence of the following ionic equilibria:

\[ \text{ClCOOC}_2\text{H}_5 + \text{B(base)} \rightarrow \text{B}_2\text{ClCOOC}_2\text{H}_5 \rightleftharpoons (\text{B}_2\text{COOC}_2\text{H}_5)^+ + \text{Cl}^- \]

Conductometric studies of solutions of Lewis acids like antimony(V) chloride, tin(IV) chloride, aluminium chloride and bromide in ethyl formate have indicated the formation of the corresponding solvates which have been actually isolated. The higher conductance of these solutions has been attributed to the existence of the ionic equilibria as:

\[ \text{L}(\text{Lewis acid}) + \text{HCOOC}_2\text{H}_5 \rightarrow \text{L}_2\text{HCOOC}_2\text{H}_5 \rightleftharpoons (\text{L}_2\text{HCOOC}_2\text{H}_4)^+ + \text{H}^+ \]

The equivalent conductance of solutions of Lewis acids in ethyl formate has been determined and consequently they have been arranged in order of decreasing strength as:

\[ \text{SbCl}_5 > \text{Sn}2\text{r}_4 > \text{SnCl}_4 > \text{TiCl}_4 \]

As strong Lewis acids cause immediate decarboxylation of ethyl chloroformate, the conductance studies of solutions of only weak Lewis acids, arsenic(III) chloride and bromide, antimony(III) chloride and bromide have been undertaken. These measurements have indicated the formation of the corresponding monosolvates and the higher conductance of their solutions has been explained as due to the following ionic equilibria:

\[ \text{L}(\text{Lewis acid}) + \text{ClCOOC}_2\text{H}_5 \rightarrow \text{L}_2\text{ClCOOC}_2\text{H}_5 \rightleftharpoons (\text{LCl})^+ + (\text{COOC}_2\text{H}_5)^+ \]
Infrared spectral studies of the adducts of Lewis acids and 1:1 molar mixtures of nitrogen organic bases with ethyl formate have been carried out. These studies have revealed the donor behaviour of carbonyl oxygen of ethyl formate to the Lewis acid molecules and the following structure has been assigned to the adducts:

\[ \text{H}^- \overset{\delta^-}{\text{L}} \overset{\delta^+}{\text{O}} \overset{\text{H}^-}{\text{C}==\text{C}_2\text{H}_5} \]

The interaction of nitrogen organic bases with ethyl formate has been visualised as through the donation of the lone pair of electrons on the nitrogen atom to the hydrogen of the ethyl group and the addition compound has been assigned the following structure:

\[ \overset{\delta^-}{\text{O}} \overset{\text{H}^-}{\text{C}==\text{C}_2\text{H}_5} \overset{\delta^+}{\text{N}} \]

The infrared spectral studies of the addition compounds of nitrogen organic bases with ethyl chloroformate have also been carried out. From the shifts observed in the stretching frequencies of various groups of ethyl chloroformate and the bases, the interaction of bases with ethyl chloroformate has been visualised as through the donation of the lone pair of electrons on the nitrogen atom of the bases to the carbonyl carbon of ethyl chloroformate and the
disappearance of (C-Cl) stretching frequency in the spectrum of the adduct has indicated the replacement of the chlorine atom of the ester with the base molecules as shown by the following configuration:

\[
\begin{array}{c}
\text{Cl} \\
\text{C} \\
\text{N}^+ \\
\text{O} \\
\end{array}
\quad \begin{array}{c}
\text{O} \\
\text{C} \\
\text{C}_6\text{H}_5\end{array}
\]

Solvolytic reactions of Lewis acids, antimony(V) chloride, tin(IV) chloride, titanium(IV) chloride, iron(III) chloride and aluminium chloride and bromide have been carried out in excess of ethyl formate. The hydrogen chloride or bromide gas liberated during the course of the solvolytic reactions has indicated the protonic nature of ethyl formate. Such studies could not be carried out in ethyl chloroformate as these Lewis acids cause its immediate decarboxylation.

Acid-base neutralisation reactions between the protonic acids, fluorosulphuric, disulphuric and sulphuric acids, the Lewis acids, antimony(V) chloride, tin(IV) chloride, tin(IV) bromide and titanium(IV) chloride and the nitrogen organic bases, pyridine, quinoline, piperidine and diethyl-aniline have been conductometrically studied in ethyl formate and the results have been confirmed potentiometrically.
In ethyl chloroformate, the acid base neutralisation reactions have been studied conductometrically and potentiometrically between the weak Lewis acids, arsenic(III) chloride, arsenic(III)bromide, antimony(III)chloride and antimony(III)bromide and the bases dimethyl and diethyl-aniline. Some of the neutralisation complexes have been actually isolated and characterised by analysis.

On the basis of these studies the two esters have been assigned the following modes of ionisation:

$$\text{HCOOC}_2\text{H}_5 \rightleftharpoons \text{H}^+ + \text{HCOOC}_2\text{H}_4^-$$

$$\text{ClCOOC}_2\text{H}_5 \rightleftharpoons (\text{COOC}_2\text{H}_5)^+ + \text{Cl}^-$$