DISCUSSION
SOLUBILITY AND SOLVATE FORMATION

Solubility

The assessment of the solubilities of various substances in a particular solvent is of vital importance as this in fact determines its utility. The solubility of various substances may also throw some light on the nature of the solvent.

The dielectric constant of the solvent controls the solubility of other substances in it to a great extent. The electrostatic forces of attraction between the cations and anions in ionic compounds keep them together. Considerable reduction of these forces facilitates the separation of the ions. By interposing a solvent of very high dielectric constant between the charged particles or by surrounding one or both of them with the solvent, the attractive forces thus are weakened, with the result that the ionisation of the solute is helped. In case the solvent has got very low dielectric constant the residual forces of attraction between the ions will still be quite pronounced, which at the most may lead to the existence of inactive ion pairs. The solubility of ionic compounds in such solvents will, therefore, be very poor. However, this is only a qualitative relationship as there are many other factors which are involved.

The energy of solvation of ions is a. other factor which is found to play an important role in the solubility of substances.
When the solvation energy exceeds interionic attractive forces and the lattice energy of the crystals, the dissolution of an ionic solute in a polar solvent takes place.

The arrangement of the ions in the solute also contributes to the solubility by exercising a polarising effect on the solvent. If the solvent is more readily polarised by the ions of a particular solute, the solubility increases.

The structural differences between organic (covalent) and inorganic (ionic) compounds suggest that the organic liquids which are usually characterised by low dielectric constants, are not suitable solvents for inorganic compounds. However, the organic liquids are excellent solvents for the compounds which are predominantly covalent in nature.

Ethyl formate and ethyl chloroformate have got low dielectric constants of 9.1 (38) and 11.3 (39) respectively. They are thus expected to be fairly good solvents for covalent compounds, but the ionic compounds may have a low solubility in them.

The solubility of various substances in ethyl formate and ethyl chloroformate has been determined at 25.0 ± 0.1°C and the results are presented in Tables II and III respectively. A consideration of Table II reveals that the electrovalent or ionic substances are practically insoluble in ethyl formate. Some of the electrovalent compounds dissolve in it, but their solubility is poor. These findings are very much in accord with the expected behaviour of ethyl formate. The solubility of the
Table XI  Solubility of different compounds in ethyl formate

<table>
<thead>
<tr>
<th>Substance</th>
<th>Solubility g./100 g.</th>
<th>Heat produced of solvent during mixing</th>
</tr>
</thead>
<tbody>
<tr>
<td>HgCl₂</td>
<td>10.950</td>
<td>Nil</td>
</tr>
<tr>
<td>Hg₄Ar₂</td>
<td>3.275</td>
<td>&quot;</td>
</tr>
<tr>
<td>HgI₂</td>
<td>1.705</td>
<td>&quot;</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>24.700</td>
<td>Considerable</td>
</tr>
<tr>
<td>SnCl₄</td>
<td>Miscible</td>
<td>&quot;</td>
</tr>
<tr>
<td>SiCl₄</td>
<td>&quot;</td>
<td>Nil</td>
</tr>
<tr>
<td>AsCl₃</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>1.171</td>
<td>&quot;</td>
</tr>
<tr>
<td>Ca₄Ar₂</td>
<td>1.104</td>
<td>&quot;</td>
</tr>
<tr>
<td>CaI₂</td>
<td>2.278</td>
<td>&quot;</td>
</tr>
<tr>
<td>BaCl₂</td>
<td>Insoluble</td>
<td>&quot;</td>
</tr>
<tr>
<td>SrCl₂</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>SbOCl₂</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>BiOCl₂</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Compound</td>
<td>Miscible</td>
<td>Nil</td>
</tr>
<tr>
<td>------------------</td>
<td>----------</td>
<td>------</td>
</tr>
<tr>
<td>SbCl₃</td>
<td>Miscible</td>
<td>Nil</td>
</tr>
<tr>
<td>SbBr₃</td>
<td>Nil</td>
<td></td>
</tr>
<tr>
<td>TiCl₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SbCl₅</td>
<td>Considerable</td>
<td></td>
</tr>
<tr>
<td>MgCl₂</td>
<td>1.634</td>
<td>Nil</td>
</tr>
<tr>
<td>MgBr₂</td>
<td>0.862</td>
<td></td>
</tr>
<tr>
<td>MgI₂</td>
<td>Insoluble</td>
<td></td>
</tr>
<tr>
<td>H₂S₂O₇</td>
<td>Miscible</td>
<td>Considerable</td>
</tr>
<tr>
<td>FSO₃H</td>
<td>Nil</td>
<td></td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>Nil</td>
<td></td>
</tr>
<tr>
<td>Cl₃CH₂COOH</td>
<td>Nil</td>
<td></td>
</tr>
<tr>
<td>Cl₃COOH</td>
<td>Nil</td>
<td></td>
</tr>
<tr>
<td>Pyridine</td>
<td>Nil</td>
<td></td>
</tr>
<tr>
<td>α-Picoline</td>
<td>Nil</td>
<td></td>
</tr>
<tr>
<td>Quinoline</td>
<td>Nil</td>
<td></td>
</tr>
<tr>
<td>Piperidine</td>
<td>Nil</td>
<td></td>
</tr>
<tr>
<td>Diethylamine</td>
<td>Nil</td>
<td></td>
</tr>
<tr>
<td>Dimethylamine</td>
<td>Nil</td>
<td></td>
</tr>
<tr>
<td>NaOC₂H₅</td>
<td>Insoluble</td>
<td></td>
</tr>
<tr>
<td>KOC₂H₅</td>
<td>Nil</td>
<td></td>
</tr>
<tr>
<td>(CH₃)₄NCl</td>
<td>Nil</td>
<td></td>
</tr>
<tr>
<td>(C₂H₅)₄NCl</td>
<td>Nil</td>
<td></td>
</tr>
</tbody>
</table>
covalent compounds particularly the Lewis acids and organic bases is fairly high. The dissolution of Lewis acids in ethyl formate is quite exothermic, which may be explained as due to the formation of adducts in solution. The protonic acids are freely miscible in ethyl formate and the heat evolved during the process of mixing is also due to the formation of addition compounds. The tertiary organic bases are also freely miscible in ethyl formate and no heat is produced during the process of mixing. The quaternary ammonium halides do not dissolve in ethyl formate. The ethoxides of alkali metals are also found to be insoluble and the latter fact helps in realising that the possibility of the formation of ethoxide ion, by the ionisation of ethyl formate is remote.

In the light of results presented in Table III, it can be inferred that the strongly ionic compounds are practically insoluble in ethyl chloroformate or if they are soluble, their solubility is low. However, the covalent compounds are fairly soluble in it. Strong Lewis acids are also miscible with ethyl chloroformate, but it has not been possible to study their solubility quantitatively as they bring about decarboxylation of the solvent and the reaction is highly exothermic. However, the weak Lewis acids like arsenic(III)chloride, arseni (III) bromide, antimony(III)chloride and antimony(III) oxide are fairly
Table III: Solubility of different compounds in ethyl chloroformate

<table>
<thead>
<tr>
<th>Substance</th>
<th>Solubility g./100 g.</th>
<th>Heat produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>HgCl₂</td>
<td>2.723</td>
<td>Nil</td>
</tr>
<tr>
<td>HgBr₂</td>
<td>8.963</td>
<td>&quot;</td>
</tr>
<tr>
<td>HgI₂</td>
<td>1.247</td>
<td>&quot;</td>
</tr>
<tr>
<td>CdCl₂</td>
<td>1.542</td>
<td>&quot;</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>1.098</td>
<td>&quot;</td>
</tr>
<tr>
<td>CaBr₂</td>
<td>1.269</td>
<td>&quot;</td>
</tr>
<tr>
<td>CaI₂</td>
<td>1.647</td>
<td>&quot;</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>1.540</td>
<td>&quot;</td>
</tr>
<tr>
<td>MgBr₂</td>
<td>1.170</td>
<td>&quot;</td>
</tr>
<tr>
<td>AsCl₃</td>
<td>Miscible</td>
<td>some heat is produced</td>
</tr>
<tr>
<td>AsBr₃</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>SbCl₃</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Diethylaniline</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Dimethylaniline</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>(C₆H₅)₄NCl</td>
<td>Insoluble</td>
<td>Nil</td>
</tr>
<tr>
<td>BaCl₂</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>SrCl₂</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>SbCl₅, AlCl₃, SnCl₄, TiCl₄ etc.</td>
<td>Decompose the solvent (65-67)</td>
<td>&quot;</td>
</tr>
<tr>
<td>HF, H₂SO₄, H₃PO₄, FS₂O₅ etc.</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Pyridine, quinoline, piperidine, α-picoline etc.</td>
<td>Form solid compounds</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
soluble and during the process of mixing, some heat is also liberated which may be ascribed to the formation of addition compounds.

The nitrogen organic bases like dimethylamine and diethylamine are also freely miscible with ethyl chloroformate. No heat is produced during the process of mixing. But the formation of the corresponding addition compounds is definitely indicated by conductance studies of their solutions in ethyl chloroformate (described in Chapter II). The solubility of other bases like pyridine, quinoline and piperidine etc. could not be determined, because of the formation of insoluble solid compounds (described in the following pages).

It may be thus concluded that ethyl formate and ethyl chloroformate are not efficient solvents for ionic compounds and only the predominantly covalent compounds are fairly soluble in them. These findings are a consequence of the low dielectric constants of the solvents.

Formation of solvates

The process of solvation (hydration is a special case of solvation in water) results in the formation of stable solvates which are compounds containing the solvent of crystallisation. The formation of solvates is not restricted to water alone. Most of the ionising solvents react with the
solutes resulting in the formation of crystalline solvates. For instance, the formation of solvates in alcohols (85), carboxylic acids (76,77), esters (30) and amides (11-14) have been reported in literature. Solvation has been explained as due to the interaction of the solute with the solvent molecule or with the ions of the solvent in such a way, that the solute either accepts electrons from or donates electrons to the solvent molecule or to the ions of the solvent.

It has been observed that generally the transition metal compounds are capable of forming such solvates, because the metal atoms in these compounds have got vacant d-orbitals, which can accommodate the additional electron pairs and acquire stable electronic configuration of the metal atoms. It is possible to predict the number of solvent molecules which may get attached to their compounds. Tin and titanium(IV) halides tend to acquire an octahedral configuration which is stable and the existence of the stable ions of the type \((\text{MX}_6)^2-\) is well known. The number of donor sites on the solvent molecule has to be considered in predicting the number of solvent molecules that may attach themselves to a particular compound. Thus it implies that two molecules of the solvent having one donor site will attach themselves to tin and titanium(IV)halides.

**Ethyl formate**

Ethyl formate is known to form monosolvates with antimony(V)chloride (44) and boron halides (42,43) while...
Solvates of Lewis acids with ethyl formate which have been isolated are presented in Table IV along with their physico-chemical characteristics.

Formation of the stable monosolvates of antimony(V) chlorides, antimony(III) chloride, antimony(III) bromide, arsenic(III) chloride, aluminium chloride and aluminium bromide may be explained as due to the tendency of metal atoms in these halides to increase their coordination number and the filling of vacant orbitals in these atoms. Measurement of specific conductance of some of the Lewis acid complexes slightly above their melting points has shown these adducts to be fairly conducting in the molten state, which points to their ionic nature. While the low conductance of the disolvate of titanium(IV) chloride in the molten state may be ascribed to the highly viscous nature of the molten complex and consequently to the decreased mobility of the ions.

The polar nature of the complexes is also supported by the high dipole moments of zirconium(IV) halide complexes with ethyl formate (4.24 D, 7.85 D and 9.3 D for \(\text{ZrI}_4 \cdot 2\text{HCOO}C_2\text{H}_5\), \(\text{ZrBr}_4 \cdot 2\text{HCOO}C_2\text{H}_5\) and \(\text{ZrCl}_4 \cdot 2\text{HCOO}C_2\text{H}_5\) respectively) (45, 52, 53).
### Table IV: Solvates of Lewis acids with ethyl formate

<table>
<thead>
<tr>
<th>Addition compound</th>
<th>Physical state</th>
<th>m.p. °C</th>
<th>Specific conductance in the molten state (ohm⁻¹cm⁻¹)</th>
<th>Molar conductance in nitrobenzene at 30° (ohm⁻¹cm²mole⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnCl₄⋅2HCOOC₂H₅</td>
<td>White solid</td>
<td>63</td>
<td>8.20 x 10⁻⁴ at 70°</td>
<td>10.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.4 x 10⁻⁴</td>
<td></td>
</tr>
<tr>
<td>TiCl₄⋅2HCOOC₂H₅</td>
<td>Colourless liquid (viscous)</td>
<td></td>
<td>0.241 x 10⁻⁴ at 25°</td>
<td>0.88</td>
</tr>
<tr>
<td>FeCl₃⋅HCOOC₂H₅</td>
<td>Reddish brown liquid</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>AlCl₃⋅HCOOC₂H₅</td>
<td>White solid (crystalline)</td>
<td>above</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>AlBr₃⋅HCOOC₂H₅</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SbCl₅⋅HCOOC₂H₅ (44)</td>
<td>-</td>
<td>135</td>
<td>32 x 10⁻³ at 140°</td>
<td>26.00</td>
</tr>
<tr>
<td>SbCl₃⋅HCOOC₂H₅</td>
<td>Colourless liquid</td>
<td>-</td>
<td>13.5 x 10⁻⁴ at 25°</td>
<td>2.26</td>
</tr>
<tr>
<td>SbBr₃⋅HCOOC₂H₅</td>
<td>Yellow solid</td>
<td>89</td>
<td>10.30 x 10⁻⁴</td>
<td>1.80</td>
</tr>
<tr>
<td>AsCl₃⋅HCOOC₂H₅</td>
<td>Colourless liquid</td>
<td>liquid</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BE₉₃⋅HCOOC₂H₅ (42)</td>
<td>Solid</td>
<td>94</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZrBr₄⋅HCOOC₂H₅</td>
<td>-</td>
<td>108</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZrX₄⋅2HCOOC₂H₅ (45-47)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

X = Cl, Br, I

* Conductance values at 25° from the conductivity versus conc. curves at the required molar ratio (details in Chapter II)

** Conductance values from the curves are also the same
Molar conductance of the milli-molar solutions of some of these solvates has been determined at 30° (Table IV) in nitrobenzene. In case of mono-solvate of antimony(V) chloride, the molar conductance has been found to be 16.0 ohm⁻¹·cm²·mole⁻¹, which shows that the complex behaves as a uni-univalent electrolyte in nitrobenzene (78). The dissolvate of tin(IV)chloride has a molar conductance of 10.5, which shows its feeble ionic character, whereas the molar conductance of other complexes is even lower, indicating that they are very feebly ionic in nitrobenzene. It is worthwhile to point out that the values of molar conductance are in close conformity with their equivalent conductance in ethyl formate (described in Chapter II).

Conductance of the solutions of fluorosulphuric and sulphuric acids and trichloroacetic acid (Chapter II) shows the formation of addition compounds in ethyl formate (Table V). But actually no solid or liquid complexes could be isolated.

Similarly, the formation of the addition compounds (Table V) of pyridine, α-picoline, quinoline and piperidine with ethyl formate has been indicated by spectrophotometrically and by means of infrared spectral studies as ried out with the solutions of these bases in ethyl formate (described in Chapter III). However, no solid or liquid adducts could be isolated.
Table V: Solvates indicated by conductance measurements

<table>
<thead>
<tr>
<th>Substance</th>
<th>Compound</th>
<th>Colour of the solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protonic acids</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorosulphonic acid</td>
<td>HSO₃⁻·HOOC₂H₅</td>
<td>Colourless</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>H₂SO₄·HOOC₂H₅</td>
<td>&quot;</td>
</tr>
<tr>
<td>Monochloroacetic acid</td>
<td>CICH₂COOH·HOOC₂H₅</td>
<td>&quot;</td>
</tr>
<tr>
<td>Dichloroacetic acid</td>
<td>Cl₂·CHCOOH·HOOC₂H₅</td>
<td>&quot;</td>
</tr>
<tr>
<td>Trichloroacetic acid</td>
<td>Cl₃C·COOH·HOOC₂H₅</td>
<td>&quot;</td>
</tr>
<tr>
<td>Nitrogen organic bases</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyridine</td>
<td>C₅H₅N·HOOC₂H₅</td>
<td>&quot;</td>
</tr>
<tr>
<td>α-Picoline</td>
<td>C₆H₇N·HOOC₂H₅</td>
<td>&quot;</td>
</tr>
<tr>
<td>Quinoline</td>
<td>C₉H₇N·HOOC₂H₅</td>
<td>&quot;</td>
</tr>
<tr>
<td>Piperidine</td>
<td>(CH₃)₅NH·HOOC₂H₅</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
Strong Lewis acids like antimony(V) chloride and aluminium chloride are known to cause the decarboxylation of ethyl chloroformate (65-67).

Weak Lewis acids like arsenic(III) chloride, arsenic(III) bromide, antimony(III) chloride and antimony(III) bromide mix with ethyl chloroformate in a slightly exothermic process. The heat evolved may be ascribed to the formation of the corresponding addition compounds which has been indicated by conductance measurements (Chapter II).

Addition compounds of ethyl chloroformate with pyridine and quinoline (64) have already been reported. Addition compounds with quinoline, piperidine, benzyl amine, p-toluidine, α-picoline, morpholine and methyl aniline have been isolated. In Table VI a detailed record of the compounds isolated along with some of their physical characteristic is being presented whereas solvates the formation of which is indicated only by conductance measurements are presented in Table VII.

Specific conductance of the monosol tes of quinoline and α-picoline has been determined at a f degrees above their melting points. Low conductance of these complexes in the molten state shows that they may have some ionic character.
<table>
<thead>
<tr>
<th>Base</th>
<th>Addition</th>
<th>Physical state</th>
<th>m.p. °C</th>
<th>Molar conductance in nitrobenzene</th>
<th>Conductance in the molten state (ohm(^{-1})cm(^{-2})mole(^{-1}))</th>
<th>Conductance in the molten state (ohm(^{-1})cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzylamine</td>
<td>C(_6)H(_5)CH(_2)NH(_2) \cdot E(_n)</td>
<td>White crystalline</td>
<td>253</td>
<td>Insoluble in nitrobenzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quinoline</td>
<td>C(_6)H(_4)N \cdot E(_n)</td>
<td>&quot;</td>
<td>75</td>
<td>0.1750</td>
<td>49 \times 10(^{-7}) at 100°C</td>
<td></td>
</tr>
<tr>
<td>(\alpha)-Picoline</td>
<td>C(_6)H(_5)N \cdot E(_n)</td>
<td>Light yellow</td>
<td>40</td>
<td>0.0808</td>
<td>60 \times 10(^{-7}) at 50°C</td>
<td></td>
</tr>
<tr>
<td>Methylalanine</td>
<td>CH(_3) \rightarrow NH \cdot 3E</td>
<td>White</td>
<td>116</td>
<td>0.1623</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Toluidine</td>
<td>C(_7)H(_5)N \cdot 3E</td>
<td>Light yellow</td>
<td>225</td>
<td>Insoluble in nitrobenzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Morpholine</td>
<td>C(_6)H(_4)O\cdot N \cdot 2E</td>
<td>White</td>
<td>177</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Piperidine</td>
<td>C(_8)H(_11)N \cdot E</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Decomposes at 127°C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

E: stands for ethyl chloroformate (C\(_\text{ClOOC}_2\text{H}_5\))
Table VII: Solvates indicated by conductance measurements

<table>
<thead>
<tr>
<th>Substance</th>
<th>Compound</th>
<th>Colour of the solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>AsCl₃·ClC₆H₄O₂</td>
<td>Colourless</td>
<td></td>
</tr>
<tr>
<td>AsBr₃·ClC₆H₄O₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SbCl₃·ClC₆H₄O₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SbBr₃·ClC₆H₄O₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₆H₅N(CH₃)₂·ClC₆H₄O₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₆H₅N(C₂H₅)₂·ClC₆H₄O₂</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Lewis acids

Nitrogen organic bases
Molar conductance of solvates of quinoline, \( \alpha \)-picoline, and methyl aniline with ethyl chloroformate has been determined at 30°C, in nitrobenzene. Very low values of molar conductance (Table VI) show that addition compounds are only feebly ionic in nitrobenzene (78).

The protonic acids have been found to cause decomposition of ethyl chloroformate and, therefore, it has not been possible to study or even indicate the formation of addition compounds with them.

Thus it may be concluded that ethyl formate forms solvates with a number of strong Lewis acids, weak Lewis acids, tertiary organic bases and the protonic acids and that the compounds are fairly polar in character. But ethyl chloroformate is found to form solvates with a limited number of weak Lewis acids and nitrogen organic bases only.
Conductance Studies of Acids and Bases in Ethyl Formate and Ethyl Chloroformate

Protonic acids in ethyl formate

The literature records many references which indicate that protonic acids display a tendency to form addition compounds with the oxygen donors like alcohols (79, 30), esters (79) and ethers (81, 82) etc. However, the formation of addition compounds between protonic acids and ethyl formate has not been studied so far. With a view to studying the formation of addition compounds of protonic acids with ethyl formate, conductance of some protonic acids in ethyl formate has been studied.

Specific conductance of the solutions of fluorosulphuric, disulphuric, sulphuric, mono, di- and tri-chloroacetic acids has been determined at 25°C in ethyl formate. In Figs. 1 and 2, the conductance of the solutions is plotted against composition as represented by acid/ester molar ratio.

In case of fluorosulphuric acid and sulphuric acid, the specific conductance goes on increasing with concentration till at the composition corresponding to 1:1 molar ratio of acid/ester, a sharp break in the curve (Fig. 1) is observed which indicates the formation of new species and the mono-solvates. In case of fluorosulphuric acid, the fall in
SPECIFIC CONDUCTANCE OF PROTONIC ACIDS IN ETHYL FORMATE AT 25°.

FIG. 1

- FLUOROSULPHUIC ACID
- DISULPHURIC ACID
- SULPHURIC ACID

MOLAR RATIO ACID/ESTER

0.2 0.4 0.6 0.8 1.0 1.4

FIG. 2

- MONOCHLOROACETIC ACID
- DICHLOROACETIC ACID
- TRICHLOROACETIC ACID

MOLAR RATIO ACID/ESTER

0.2 0.4 0.6 0.8 1.0 1.4
conductance beyond 1:1 molar ratio may be attributed to the increased viscosity of the system or to the decreased mobility of the ions.

The curve representing the conductance of sulphuric acid in ethyl formate shows an increase in conductance beyond the acid/ester molar ratio of 1:1 which may be due to the presence of excess of sulphuric acid which has conductance of $1.04 \times 10^{-2} \text{ ohm}^{-1} \text{cm}^{-1}$ at $25^\circ$ in the pure state.

The conductance of disulphuric acid in ethyl formate, could not be determined beyond the acid/ester molar ratio of 0.4, because beyond this point the solvent starts decomposing. However, the addition of the acid to ethyl formate shows an increase in conductance which indicates the formation of some new species (of the addition compound between disulphuric acid and ethyl formate) which is more ionic in nature than either ethyl formate or disulphuric acid.

In Fig. 2 the plots of conductance of solutions of mono, di and trichloroacetic acids versus the acid/ester molar ratio are presented. In each case the conductance goes on increasing regularly with the addition of acids to the solvent, till a break is observed at acid/ester molar ratio of 1:1 which indicates the formation of monosolvates of halogen substituted acetic acids with ethyl formate.

The specific conductance of fluorosulphuric and sulphuric acids are $7 \times 10^{-4}$ and $1.04 \times 10^{-2} \text{ ohm}^{-1} \text{cm}^{-1}$ respectively at $25^\circ$. Mono, di and trichloroacetic acids have
Specific conductance of the pure solvent is quite low.

Specific conductance of the mixtures of protonic acids is higher than that of sulphuric acid. The specific conductance of the mixture of sulphuric acid in ethyl formate is quite significant. Fairly high conductance of the solutions of protonic acids in ethyl formate suggests that the addition compounds are fairly ionic in nature.

As ethyl formate is basic in nature, the protons furnished by the protonic acids are solvated by it. The higher conductance of the solutions may, therefore, be due to the following ionic equilibria:

\[
HX + HCOOC_2H_5 \rightarrow (HCOOC_2H_5HX) \rightleftharpoons (HCOOC_2H_5)_+ + X^- \quad \ldots (1)
\]

(HX stands for the protonic acids)

The conductance of the addition compounds of protonic acids with ethyl formate (taken from the plots) is given in Table VIII.

The relative strength of protonic acids has been compared in acetic acid by determining the equivalent conductance in low concentration range in acetic acid by Kolthoff and Willman (9) and Emelius and coworkers (83). Quite
Table VIII: Conductance of the addition compounds of protonic acids

<table>
<thead>
<tr>
<th>Acid</th>
<th>Compound</th>
<th>Sp. conductance (read from graph)</th>
<th>Sp. conductance of the pure acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSO₃H</td>
<td>FSO₃H.HCCOC₂H₅</td>
<td>1.49 x 10⁻²</td>
<td>2 x 10⁻⁴ at 25⁰</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>H₂SO₄.HCCOC₂H₅</td>
<td>7.80 x 10⁻³</td>
<td>1.04 x 10⁻² at 25°</td>
</tr>
<tr>
<td>ClCH₂COOH</td>
<td>ClCH₂COOH.HCCOC₂H₅</td>
<td>7.70 x 10⁻⁶</td>
<td>14 x 10⁻⁷ at 60°</td>
</tr>
<tr>
<td>Cl₂CHCOOH</td>
<td>Cl₂CHCOOH.HCCOC₂H₅</td>
<td>8.70 x 10⁻⁶</td>
<td>7 x 10⁻⁸ at 25°</td>
</tr>
<tr>
<td>Cl₃CCOOH</td>
<td>Cl₃CCOOH.HCCOC₂H₅</td>
<td>9.9 x 10⁻⁶</td>
<td>3 x 10⁻⁹ at 60°</td>
</tr>
</tbody>
</table>

recently Paul et al (loc cit) have compared the relative strength of fluorosulphuric acid with perchloric acid in acetic acid by measuring their equivalent conductance at low concentration by the potential jumps while carrying out potentiometric titrations with a particular base. Gillespie and coworkers(84) have compared the relative strength of a number of protonic acids in anhydrous sulphuric acid. No attempt seems to have been made to arrive at such quantitative results in other solvents except for Paul and Malhotra (30) who have compared the relative strength of fluorosulphuric, chlorosulphuric, p-toluene sulphuric, disulphuric acids and trichloro-, monochloro- and acetic acids in ethyl acetate which has a low dielectric constant(6.4 at 20⁰)
by measuring the conductance of their solutions.

In order to compare the relative strength of fluorosulphuric, disulphuric, sulphuric, hydrobromic and hydrochloric acids in ethyl formate, equivalent conductance of their solutions has been determined at $25^\circ$ and is plotted against the square root of concentration ($\sqrt{c}$) in the low concentration range ($1.25 \times 10^{-4}$ g.eq./litre) (Fig. 3). Values of equivalent conductance at infinite dilution ($\lambda_0$) have been obtained by extrapolating the curves to zero concentration and are presented in Table IX.

**Table IX**: The equivalent conductance of protonic acids at infinite dilution ($\lambda_0$)

<table>
<thead>
<tr>
<th>Acid</th>
<th>Equivalent conductance at infinite dilution ($\lambda_0$)</th>
</tr>
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<tbody>
<tr>
<td>$\text{FSO}_3\text{H}$</td>
<td>9.0</td>
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<tr>
<td>$\text{H}_2\text{S}_2\text{O}_7$</td>
<td>6.1</td>
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<tr>
<td>$\text{H}_2\text{SO}_4$</td>
<td>5.0</td>
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<tr>
<td>$\text{HBr}$</td>
<td>4.5</td>
</tr>
<tr>
<td>$\text{HCl}$</td>
<td>3.25</td>
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</table>

On the basis of these values these protonic acids may be arranged in decreasing order of strength as:

$\text{FSO}_3\text{H} > \text{H}_2\text{S}_2\text{O}_7 > \text{H}_2\text{SO}_4 > \text{HBr} > \text{HCl}$
FIG. 3 EQUIVALENT CONDUCTANCE OF PROTONIC ACIDS IN ETHYL FORMATE AT 50°
However, it may be mentioned that the values of equivalent conductance are only approximate as it involves the extrapolation of $\lambda_0$ against $\sqrt{c}$ curve to zero concentration. Keeping in view the low dielectric constant of the solvent and very small difference in the values of $\lambda_0$ (equivalent conductance at infinite dilution) as quoted earlier, it is worthwhile to point out that the order of relative strength of these acids may not be very conclusive.

**Protonic acids in ethyl chloroformate**

As the protonic acids cause decarboxylation of ethyl chloroformate, the conductance studies of the protonic acids in ethyl chloroformate could not be carried out.

**Nitrogen organic bases in ethyl formate**

The nitrogen organic bases like pyridine, $\alpha$-picoline, piperidine and benzyl amine are expected to act as solvo bases, because of the presence of a lone pair of electrons on the nitrogen atom which can be easily donated. These bases mix with ethyl formate in all proportions and practically no heat is liberated during the process. With a view to study the nature of the solutions of these bases in ethyl formate, their specific conductance in ethyl formate has been determined at $25^\circ$ and is plotted against composition as represented by the molar ratio of base/ester (Fig. 4).
FIG. 4 SPECIFIC CONDUCTANCE OF B SES IN ETHYL FORMATE AT 25°C.
The conductance of the solutions of bases in ethyl formate goes on increasing with concentration till a break is observed at the composition represented by the molar ratio of base/ester as 1:1 which indicates the formation of the monosolvates. Beyond the composition represented by the molar ratio of base/ester as 1:1, there is a change in the slope of the curve due possibly to the increased viscosity of the system or to dilution effect. An increase in conductance of the solutions indicates the formation of the monosolvates which are more ionic than either of the components and are responsible for the higher conductance of the system. Since the conductance is quite low to further substantiate the conclusions, I.R. studies have been carried out which confirm the formation of adducts between these two components (described in Chapter III).

It is worthwhile to point out that the conductance of these solutions is much lower than that of the solutions of protonic acids. This may be ascribed to the basic nature of the pure solvent which is, a poor proton donor and good proton acceptor. The conductance of the solutions of bases may be explained by assuming the solvent to be a proton donor or an acid. This condition is very much exaggerated due to the addition of strong bases (proton acceptors) like piperidine etc. and protonated base molecules result. Thus the conductance of the solutions of the bases in ethyl formate may be ascribed to protonation of the bases by ethyl formate.
In order to throw more light on the nature of the solutions of nitrogen organic bases in ethyl formate, equivalent conductance of \(\alpha\)-picoline, quinoline, diethyl aniline and piperidine has been determined in ethyl formate at 25°C. The plots of equivalent conductance \(\lambda_0\) versus square root of concentration \(\sqrt{c}\) in the low concentration range \((1-25 \times 10^{-4}\) g.eq./litre) are presented in Fig. 5. By extrapolating the curves to zero concentration, equivalent conductance at infinite dilution \(\lambda_0\) has been computed. The values of \(\lambda_0\) (equivalent conductance at infinite dilution) obtained for piperidine, \(\alpha\)-picoline, quinoline and diethyl-aniline are 0.87, 0.80, 0.68 and 0.61 respectively. On the basis of these values which are only approximate, these bases may be arranged in order of decreasing strength as:

\[
\text{Piperidine} > \alpha\text{-picoline} > \text{quinoline} > \text{diethyl-aniline}
\]

However, it is worth mentioning that in view of low dielectric constant of the solvent and very slight difference in the values of equivalent conductance, this arrangement of the bases in the decreasing order of strength may not be very conclusive.

The low specific conductance, equivalent conductance, and limiting conductance of the bases in ethyl formate is not surprising in view of the basic character of the solvent itself, as in the same solvent limiting conductance of the protonic acids is many times higher.
FIG. 5 EQUIVALENT CONDUCTANCE (c) OF BASES IN ETHYL FORMATE AT 25°.

- ○ ○ - α PI OLINE
- △ △ - QUI OLINE
- □ □ - DIET YLANILINE
- × × - PIP RIDINE

CONCENTRATION g. eq/litre (\times 10^2)

EQUIVALENT CONDUCTANCE A_\text{c}

0.2 0.4 0.6 0.8 1.0 1.2 1.4

1 2 3 4 5 6 7
In view of these observations, however, it may be inferred that the solvent brings about the protonation of the bases to some extent and the increase in conductance may be explained as due to the existence of the ionic equilibria as represented below:

$$B + HCOOC_2H_5 \rightarrow (B.HCOOC_2H_5) \leftrightarrow BH^+ + (HCOOC_2H_4)^-$$

(11)

(B stands for the base) or $$\leftrightarrow BH^+ + (COOC_2H_5)^-$$ ... (iiia)

The infrared spectral studies (described in Chapter III) carried out with 1:1 molar mixtures of ethyl formate with bases favour the ionisation of the adduct as represented by equation (ii) and not by equation (iiia). In view of the ionisation of the adduct (base + ethyl formate) as represented by equation (ii) ethyl formate may ionise as:

$$HCOOC_2H_5 \leftrightarrow H^+ + HCOOC_2H_4^-$$  .... (iii)

As a proton can rarely lead an independent existence, it gets solvated by solvent molecule:

$$H^+ + HCOOC_2H_6 \rightarrow (H.HCOOC_2H_6)^+$$  .... (iv)

Thus the overall ionisation of ethyl formate may be represented as:

$$2HCOOC_2H_5 \leftrightarrow (H.HCOOC_2H_6)^+ + HCOOC_2H_4^-$$  .... (v)
Nitrogen organic bases in ethyl chloroformate

It has been mentioned earlier that the interaction of nitrogen organic bases with ethyl chloroformate results in the formation of addition compounds which are insoluble in ethyl chloroformate. Conductance of the solutions of quinoline, piperidine, α-picoline, p-toluidine, benzyl amine and methyl-aniline in ethyl chloroformate, therefore, could not be measured.

However, dimethyl and diethyl aniline have been found to be freely miscible with ethyl chloroformate. With a view to throwing light on the nature of their solutions in ethyl chloroformate, specific conductance of these bases in ethyl chloroformate has been determined at 25°C. With the first addition of a small quantity of base to ethyl chloroformate, the conductance of the resulting solution increases. However, further additions of the base do not cause any further significant increase in conductance possibly due to the formation of ion pairs. The conductance of 1:1 molar mixtures of these bases with ethyl chloroformate has been determined and has been found to be $3.5 \times 10^{-6}$ ohm$^{-1}$cm$^{-1}$ and $6.9 \times 10^{-6}$ ohm$^{-1}$cm$^{-1}$ for diethyl and dimethyl aniline respectively. The conductance of the 1:1 molar mixtures of bases with ethyl chloroformate is higher than the conductance of either of the components and thus points to an interaction
of bases with ethyl chloroformate resulting in the formation of ionic species in solutions.

Ethyl chloroformate has been reported to react with silver nitrate (60) resulting in the replacement of chlorine atom with nitro group which suggests, that in ethyl chloroformate the chlorine atom is labile. The hydrolysis reaction of ethyl chloroformate has also been visualised through the existence of the cation (COOC₂H₅)⁺ (63). Keeping in view the lability of chlorine atom, the higher conductance of the solutions of bases in ethyl chloroformate may be explained as due to the formation of the solvates which are ionic in nature. The conductance of the solutions may, therefore, be explained as due to the following ionic equilibria:

\[ B(\text{base}) + (\text{ClCOOC}_₂\text{H}_₅) \rightarrow B\text{ClCOOC}_₂\text{H}_₅ \]

\[ (B\text{ClCOOC}_₂\text{H}_₅)^+ + \text{Cl}^- \quad \ldots \ldots \quad \text{(vi)} \]

which implies that the ethyl chloroformate may be assigned the possible mode of ionisation as:

\[ \text{ClCOOC}_₂\text{H}_₅ \leftrightarrow \text{Cl}^- + (\text{COOC}_₂\text{H}_₅)^+ \quad \ldots \ldots \quad \text{(vii)} \]

This mode of ionisation has been further substantiated with the help of infrared spectral studies (described in Chapter III) carried out with the addition compounds of bases with ethyl chloroformate.
Lewis acids in ethyl formate

As has been described in the preceding section, interaction of Lewis acids with ethyl formate results in the formation of stable solvates (addition compounds). Specific conductance of some of them in the molten state indicates that they are fairly ionic in nature. With a view to suggesting the possible mode of ionisation of ethyl formate and also to throw light on the nature and composition of solvates which have been isolated, conductance of the solutions of Lewis acids in ethyl formate has been measured at 25°. Specific conductance of the solutions of antimony(V) chloride, tin(IV) chloride, iron(III) chloride, aluminium chloride, aluminium bromide, arsenic(III) chloride, antimony(III) chloride and bromide in ethyl formate has been determined at 25° and is plotted against concentration as represented by the acid/ester molar ratio (Figs. 6, 7).

Ethyl formate has a very low specific conductance. The Lewis acids are also either non-conducting or possess very low conductance (88). But the conductance of solutions of Lewis acids in ethyl formate is much higher than either of the components which indicates the greater ionic nature of the adducts formed. A similar conclusion has been drawn from the conductance of some of the complexes in the molten state (Table IV).
Figure 6 indicates that the specific conductance of the solutions of weak Lewis acids in ethyl formate goes on increasing till at the acid/ester molar ratio of 1:1, a sharp break in the curve is observed. At higher concentrations the conductance begins to decrease with increase in concentration. The break at 1:1 molar ratio in the case of arsenic(III) chloride, antimony(III)chloride and antimony(III)bromide confirms the composition of monosolvates with ethyl formate which have been actually isolated and are described in the preceding chapter. The increase in conductance may be due to the ionic nature of the addition compounds formed. The fall in conductance beyond the acid/ester molar ratio of 1:1, may be explained as due to the increased viscosity of the system and consequently to the decreased mobility of the ions or to dilution effect. However, it is worth-mentioning that specific conductance of the monosolvates as found from the plots roughly corresponds to the conductance of these solvates in the molten state (Table IV).

Figure 7 represents the plots of specific conductance of the Lewis acids tin(IV)chloride, antimony(V)chloride, iron(III)chloride, aluminium chloride and aluminium bromide versus composition as represented by the acid/ester molar ratio.

The plot of specific conductance of tin(IV)chloride solution in ethyl formate against composition indicates three
FIG.6 SPECIFIC CONDUCTANCE OF LEWIS ACIDS IN ETHYL FORMATE AT 25°C.

- ○ ○ ANTIMONY (III) CHLORIDE
- • • ANTIMONY (III) BROMIDE
- □ □ ARSENIC (III) CHLORIDE

SPECIFIC CONDUCTANCE $\times 10^5$

MOLAR RATIO ACID/ESTER

0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6

SPECIFIC CONDUCTANCE $\times 10^6$ (AsCl$_3$)
FIG. 7 SPECIFIC CONDUCTANCE OF ETHYL FORMATE AT 25°

- MOLAR RATIO SnCl₄ HCOOEt
  - 0.2 0.4 0.6 0.8 1.0 1.0 1.1 1.4
- TIN (IV) CHLORIDE
- ANTIMONY (V) CHLORIDE
- IRON (III) CHLORIDE
- ALUMINIUM CHLORIDE
- ALUMINIUM BROMIDE

SPECIFIC CONDUCTANCE X 10⁻³

MOLAR RATIO ACID/ESTER

0.1 0.2
breaks corresponding to composition as represented by the molar ratio acid/ester of 1:4 and 1:2 and 1:1 respectively. Formation of monosolvates can be explained on the basis of penta coordination of tin (II) while that of the disolvate can be explained on the basis of its hexa coordination. Tetrasolvate, the formation of which has been indicated conductometrically, could not be actually isolated. One of the possible ways of explaining the formation of this compound could be on the basis of hexa coordination of tin. The disolvate so formed may be further solvated by two additional molecules of the solvent. However, it is very difficult to say anything conclusively about its structure without any further evidence.

Conductance of solutions of aluminium chloride and bromide, antimony(V)chloride and iron(III)chloride in ethyl formate could not be measured over a wide range because of the separation of the solid adducts (Fig. 7). However, their solutions in ethyl formate have been found to be fairly conducting. The solid adducts separating out during the course of the conductance measurements, on being analysed have been found to be the corresponding monosolvates and their formation has already been explained as due to the tendency of the metal atoms in these Lewis acids to increase their coordination number by one.

In view of the proposed ionisation of ethyl formate as represented by equation (iii), the higher conductance of
the solutions of Lewis acids in ethyl formate can be explained on the basis of formation and ionisation of the adducts as:

\[
\begin{align*}
\text{AsCl}_3 + \text{HCOOC}_2\text{H}_5 & \rightarrow \text{AsCl}_3\cdot\text{HCOOC}_2\text{H}_5 \rightleftharpoons \text{H}^+\cdot(\text{HCOOC}_2\text{H}_4\cdot\text{AsCl}_3)^- \\
\text{SbCl}_3 + \text{HCOOC}_2\text{H}_5 & \rightarrow \text{SbCl}_3\cdot\text{HCOOC}_2\text{H}_5 \rightleftharpoons \text{H}^+\cdot(\text{HCOOC}_2\text{H}_4\cdot\text{SbCl}_3)^- \\
\text{SbCl}_5 + \text{HCOOC}_2\text{H}_5 & \rightarrow \text{SbCl}_5\cdot\text{HCOOC}_2\text{H}_5 \rightleftharpoons \text{H}^+\cdot(\text{HCOOC}_2\text{H}_4\cdot\text{SbCl}_5)^- \\
\text{AlCl}_3 + \text{HCOOC}_2\text{H}_5 & \rightarrow \text{AlCl}_3\cdot\text{HCOOC}_2\text{H}_5 \rightleftharpoons \text{H}^+\cdot(\text{HCOOC}_2\text{H}_4\cdot\text{AlCl}_3)^- \\
\text{FeCl}_3 + \text{HCOOC}_2\text{H}_5 & \rightarrow \text{FeCl}_3\cdot\text{HCOOC}_2\text{H}_5 \rightleftharpoons \text{H}^+\cdot(\text{HCOOC}_2\text{H}_4\cdot\text{FeCl}_3)^- \\
\text{SnCl}_4 + 2\text{HCOOC}_2\text{H}_5 & \rightarrow \text{SnCl}_4\cdot 2\text{HCOOC}_2\text{H}_5 \rightleftharpoons 2\text{H}^+\cdot(\text{HCOOC}_2\text{H}_4\cdot\text{SnCl}_4)^- \\
\text{SnCl}_4 + \text{HCOOC}_2\text{H}_5 & \rightarrow \text{SnCl}_4\cdot\text{HCOOC}_2\text{H}_5 \rightleftharpoons \text{H}^+\cdot(\text{HCOOC}_2\text{H}_4\cdot\text{SnCl}_4)^- 
\end{align*}
\]

However, in view of Drago's findings (67) that FeCl$_4^-$ ion exists in solutions of iron(III)chloride in triethylphosphosphate which does not contribute any Cl$^-$ ions, other modes of ionisation based upon coordination model may be suggested as:

\[
\begin{align*}
2(\text{AsCl}_3\cdot\text{HCOOC}_2\text{H}_5) & \rightleftharpoons (\text{AsCl}_2\cdot 2\text{HCOOC}_2\text{H}_5)^+ + \text{AsCl}_4^- \quad \text{...(xv)} \\
2(\text{SbCl}_3\cdot\text{HCOOC}_2\text{H}_5) & \rightleftharpoons (\text{SbCl}_2\cdot 2\text{HCOOC}_2\text{H}_5)^+ + \text{SbCl}_4^- \quad \text{...(xvi)} 
\end{align*}
\]
This mode of ionisation does not consider the ionisation of the solvent as a pre-requisite for the ionisation of the adducts.

The data available with us for the present is insufficient to reject one mode of ionisation in favour of the other. However, in the present discussion the mode of ionisation as represented by the solvent system concept is being taken into account.

The ionic nature of the complexes is further substantiated by carrying out electrolysis of the solutions of antimony(V)chloride and tin(IV)chloride in ethyl formate. No gas is liberated on the cathode, but the drift of the metal ions towards the anode indicates that the Lewis acids form a part of the anion. The above mentioned mode of ionisation, has also been substantiated by the help of infrared spectral studies of the complexes of Lewis acids with ethyl formate (described in Chapter III).

The equivalent conductance of solutions of Lewis acids antimony(V)chloride, tin(IV)chloride and bromide and titanium(IV)chloride has been determined in ethyl formate at 25°, and is plotted against the square root of concentration.
These curves have been extrapolated to zero concentration to obtain approximate values of equivalent conductance at infinite dilution ($\lambda_0$). The $\lambda_0$ values of 32.0, 13.0, 14.0 and 8.0 for antimony(V) chloride, tin(IV) bromide, tin(IV) chloride, and titanium(IV) chloride respectively have been obtained. In order to get more correct values of ($\lambda_0$), the plots of $c \lambda_C$ versus $1/\lambda_C$ have been constructed. In the case of antimony(V) chloride and tin(IV) bromide only, the plots are straight lines, (Fig. 9). From the intercept of these lines on $1/\lambda_C$ axis, corrected values of $\lambda_0$ have been obtained as 28.6 and 17.2 respectively for these two compounds. On the basis of their equivalent conductance, these Lewis acids may be arranged in the order of decreasing strength as:

$$\text{SbCl}_5 > \text{SnBr}_4 > \text{SnCl}_4 > \text{TiCl}_4$$

The infrared spectral studies (described in Chapter III) of the addition compounds of these Lewis acids with ethyl formate have also substantiated the above order of relative strength of the acids.

Equivalent conductance at infinite dilution ($\lambda_0$), for Lewis acids is comparatively higher than that for protonic acids in ethyl formate. It is, therefore, reasonable to assume that the Lewis acids react with the solvent to form adducts which ionise to give highly mobile protons. The alternative ionisation involving the formation of Cl⁻ ions is less probable.
FIG. 8 EQUIVALENT CONDUCTANCE OF L WIS ACIDS IN ETHYL FORMATE AT 25°C.
FIG. 9

(PLOTS OF $c\lambda c$ vs $1/\lambda c$)

$I$ SbCl$_5$, $\lambda_0 = 28.6$

$II$ SnBr$_4$, $\lambda_0 = 17.2$
as the ionic mobility of the Cl$^-$ ions is less than the H$^+$ ions. Higher values of equivalent conductance of Lewis acids as compared to protonic acids in ethyl formate does not necessarily mean that the protonic acids are weaker acids than the Lewis acids. Indeed, the comparison is not very useful in view of different nature of the reactions involved in the two cases.

**Lewis acids in ethyl chloroformate**

Strong Lewis acids like antimony(V)chloride and aluminium chloride are known to cause decarboxylation of ethyl chloroformate (65-67) and hence conductance of the solutions of these Lewis acids in ethyl chloroformate could not be measured. Weak Lewis acids like arsenic(III)chloride, arsenic(III)bromide, antimony(III)chloride and antimony(III) bromide are freely miscible with ethyl chloroformate in an exothermic reaction and this has been ascribed to the formation of addition compounds.

With a view to throwing more light on the nature of these addition compounds and also to support the mode of ionisation of ethyl chloroformate as already suggested, the specific conductance of the solutions of these Lewis acids in ethyl chloroformate has been determined at 25°C and is plotted against composition as represented by theolar ratio of acid/ester (Figs. 10, 11).

The conductance of the mixtures is increasing regularly with the addition of the acids to the solvent, till
FIG. 10 SPECIFIC CONDUCTANCE OF LEWIS ACIDS IN ETHYL CHLOROFORMATE AT 25 °C.

-○- ARSENIC (III) CHLORIDE (\(\sigma^7\))
-△- ARSENIC (III) BROMIDE (\(\sigma^6\))

SP. CONDUCTANCE

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<th>Value</th>
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<td>1.1</td>
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<td>1.2</td>
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<td>1.3</td>
</tr>
</tbody>
</table>

MOLAR RATIO ACID/ESTER
FIG II SPECIFIC CONDUCTANCE OF LEWIS ACIDS IN ETHYL CHLOROFORMATE AT 25°C.

- O - ANTI ONY(III) CHLORIDE
- △ - ANTI ONY (III) BROMIDE

\[ \sigma = \text{CONDUCTANCE} \times 10^5 (\text{ohm}^{-1} \text{cm}^{-1}) \]

-0.5  0.1  0.15  0.2  0.25  0.3  0.35  0.4

MOLAR RATIO ACID/ESTER
at the molar ratio of acid/ester as 1:1, a break in the conductance curve is observed. Beyond this point, the conductance starts decreasing which may be explained as due to the increased viscosity of the system or consequently to the decreased mobility of the ionic species or to dilution effect since the Lewis acids themselves have a low conductance.

It has been described earlier that the conductance of the solvent is very low and that the Lewis acids themselves are also either non-conducting or their conductance is very poor (85). The higher conductance of the mixtures of Lewis acids and ethyl chloroformate may, therefore, be explained as due to the formation of the addition compounds, which may be ionic in nature.

In view of the proposed ionisation of ethyl chloroformate as represented by equation (vii), the higher conductance of the system may be explained as due to the existence of the following ionic equilibria:

\[ L + \text{COOC}_2\text{H}_5 \rightarrow (L\cdot\text{COOC}_2\text{H}_5) \rightleftharpoons \text{Cl}^+ + (\text{COOC}_2\text{H}_5)^- \] ...(xx)

(where L stands for Lewis acids AsCl₃, AsBr₃, SbCl₅ and SbBr₅).

Thus the weak Lewis acids interact with ethyl chloroformate forming the adducts which on ionisation produce cations characteristic of the solvent. This behaviour is quite justified in view of the Smith's definition of acids. However, the alternative mode of ionisation of these adducts based upon coordination model can be represented by the following equation:
\[ 2(MCl_3\cdot ClCOOC_2H_5) \rightleftharpoons (MCl_2\cdot 2ClCOOC_2H_5)^+ + MCl^- \] 

(where \( M \) stands for metal atoms As and Sb)

But the mode of ionisation of the adducts based upon the solvent system concept, is being taken into account, during the subsequent discussion.
Attempts have already been made to throw light on the structure of the addition compounds of Lewis acids with ethyl formate. Raman spectral studies of the mixtures of tin(IV) chloride with ethyl formate indicate a shift in the carbonyl stretching frequency pointing to the donor function of the carbonyl oxygen. The addition compound has thus been assigned the following structure:

```
\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{H} & \quad \text{O} \quad \text{Sn} \quad \text{C} \\
\text{O} & \quad \text{R} \quad \text{Cl} & \quad \text{Cl}
\end{align*}
\]
```

The infrared spectral studies of the mixtures of antimony(III) chloride and tin(IV) chloride with ethyl formate in ethylene dichloride solution have also revealed that the stretching frequencies of (C = O) and (C - O) groups present in ethyl formate undergo perturbation on complex formation \((56, 57)\) and this has been ascribed to the donation of electrons by the carbonyl oxygen. Similar results have also been arrived by Lappert \((88)\) on the basis of infrared spectral studies for the adducts of ethyl acetate.

In the preceding section, the formation of addition compounds of Lewis acids with ethyl formate and the results of conductance studies carried out with these adducts have been
described. With a view to throwing more light on the structure
of these complexes, infrared spectral studies of the adducts of
tin(IV)chloride, titanium(IV)chloride, antimony(V)chloride,
iron(III)chloride, aluminium chloride and bromide with ethyl
formate have been carried out. The results obtained are
being presented here.

Table X presents a detailed record of the I.R. spectra
of ethyl formate and its complexes with Lewis acids.

The absorption bands at 2987 cm\(^{-1}\) and 2930 cm\(^{-1}\) in the
I.R. spectrum of pure ethyl formate are assigned to (C-H)
stretching modes of vibration (89), a strong band at 1750 cm\(^{-1}\),
is assigned to the carbonyl stretching frequency (89) and
those at 1190 cm\(^{-1}\) and 1010 cm\(^{-1}\) may be assigned to the (CO-O)
and (O-C\(_2\)H\(_5\)) stretching frequency (loc cit).

The absorption frequencies observed in the spectrum
of ethyl formate undergo appreciable perturbation on complex
formation with Lewis acids. The principal features of the
spectrum of Lewis acid complexes, as compared to the spectrum
of pure ethyl formate may be summed up as follows:

i) The (C-H) stretching frequencies at 7 and 2930 cm\(^{-1}\) in
ethyl formate shift to the lower spectral region of
2876-2896 cm\(^{-1}\) and 2820-2860 cm\(^{-1}\) respectively.

ii) The carbonyl stretching frequency (17 cm\(^{-1}\)) in ethyl
formate shifts to the lower spectral region of 1635-1660 cm\(^{-1}\)
which may be ascribed to \(\nu(C=O)\) str.

\[\]
<table>
<thead>
<tr>
<th>Ethyl formate</th>
<th>Assignment</th>
<th>$\nu (\text{cm}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\cdot$SbCl$_5$HCOO$_2$H$_5$ $\cdot$SnCl$_4$2HCOO$_2$H$_5$TiCl$_4$2HCOO$_2$H$_5$FeCl$_3$HCOO$_2$H$_5$AlCl$_3$HCOO$_2$H$_5$AlBr$_3$HCOO$_2$H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(solid)</td>
<td>(solid)</td>
<td>(liquid)</td>
</tr>
<tr>
<td>2997 v.v.</td>
<td>$\nu (\text{C-H})$</td>
<td>2940 v.s.</td>
</tr>
<tr>
<td>2930 sh-</td>
<td>stretching</td>
<td>2860 sh.</td>
</tr>
<tr>
<td>1750 s</td>
<td>$\nu (\text{C=O})$</td>
<td>1715 s</td>
</tr>
<tr>
<td></td>
<td>1630 s</td>
<td>1630 s</td>
</tr>
<tr>
<td></td>
<td>1600 s</td>
<td></td>
</tr>
<tr>
<td>1380 m</td>
<td>$\delta (\text{C-H})$</td>
<td>1345 s</td>
</tr>
<tr>
<td>1305</td>
<td>1315 m</td>
<td>1310 m</td>
</tr>
<tr>
<td>1290 v.s.</td>
<td>(CO-O)</td>
<td>1270 v.</td>
</tr>
<tr>
<td>or (CO=O)</td>
<td>1230 b.</td>
<td></td>
</tr>
<tr>
<td>1010 s</td>
<td>(O=C$_2$H$_5$)</td>
<td>1150 m</td>
</tr>
<tr>
<td>or (O=C$_2$H$_5$)</td>
<td>1110 m</td>
<td>1060 m</td>
</tr>
<tr>
<td></td>
<td>990 s</td>
<td>1000 s</td>
</tr>
<tr>
<td>840 v.v.</td>
<td>845 s.</td>
<td>850 s.</td>
</tr>
<tr>
<td>750 v.v.</td>
<td>765 m.</td>
<td>790 v.</td>
</tr>
<tr>
<td>685</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$s =$ strong; $v.s.$ = very strong; $v.$ = weak; $v.v.$ = very weak; $m.$ = medium; $b.$ = broad; sh = shoulder.
iii) The stretching frequency at 1290 cm\(^{-1}\) assigned to \(\nu(CO-O)\) in ethyl formate, shifts to the higher spectral region of 1275-1280 cm\(^{-1}\), corresponding to \(\nu(CO-O)\) group.

iv) The stretching frequency of \((O-C_2H_5)\) group gets slightly displaced from 1010 cm\(^{-1}\) in ethyl formate to 1190-1150 cm\(^{-1}\) in the complex.

v) Conspicuous changes are also observed in the \((C-H)\) deformation frequencies.

Due to higher electronegativity of oxygen, the electron density centres on the carbonyl oxygen atom as shown below:

\[
\begin{align*}
H - C\bigg\langle 0 \bigg\rangle & \rightleftharpoons H - C\bigg\langle 0 \bigg\rangle \\
0 - C_2H_5 & \rightleftharpoons 0 - C_2H_5
\end{align*}
\]

In the presence of a Lewis acid, the non-bonding electron cloud on the carbonyl oxygen shifts to the vacant orbitals of the metal atom of the Lewis acid and this causes a drag of electrons on ethereal oxygen. On complexing with Lewis acids a decrease in the force constant and bond order of \((C=O)\) bond along with simultaneous increase in the bond order of \((O-C)\) bond is, therefore, expected which is depicted by lowering of \(\nu(C=O)\) and an increase in \(\nu(C-O)\) of esters. As the spectral changes indicated by ethyl formate on complex formation are in agreement with the above consideration, the possible structure of the addition compounds
may be represented as:

\[
\begin{array}{c}
\text{L} \\
\text{C} \\
\text{H}_5
\end{array}
\]

(\text{where L stands for Lewis acids})

The above mode of interaction involving the donation of electrons by the carbonyl oxygen and not by ethereal oxygen is well known in many other compounds (88, 90). An increase in the stretching frequency of \((\text{C} = \text{C}_2\text{H}_5)\) group indicates that a carbon atom of \(\text{C}_2\text{H}_5\) group has acquired a relatively more positive character. This positive charge results in one of the hydrogen atoms becoming more labile. The infrared spectral studies carried out with the adducts of Lewis acids with formamide by Paul et al have also shown that in the complex, the hydrogen of the formyl group is not affected whereas the hydrogen of \(\text{NH}_2\) group in formamide becomes more labile (90).

It has been described in an earlier section that the solutions of Lewis acids in ethyl formate are fairly conducting and this has been ascribed to the ionic nature of the addition compounds formed. In view of the above mentioned structure of the adduct in which the hydrogen of ethyl group is supposed to have become more labile, the adduct may be assigned the following mode of ionisation:
Since the conductance is not very high the adduct may be largely undissociated or present as $L\cdot HCOOC_2H_5$. The above mode of interaction of Lewis acids with ethyl formate and the subsequent ionisation of the adduct, thus supports the mode of ionisation of ethyl formate, which has been described earlier (equations iii, iv and v).

The relative strength of the Lewis acids with respect to ethyl formate as the reference base, is reflected by the lowering of carbonyl stretching frequency. As indicated in Table X, antimony(V) chloride shows a maximum of displacement of 150 cm$^{-1}$ in the carbonyl stretching frequency. On this basis, the Lewis acids forming the complexes of same stoichiometry may be arranged in the decreasing order of strength as:

$$\begin{align*}
SbCl_5 & > FeCl_3 > AlCl_3 > AlBr_3 \\
SnCl_4 & > TiCl_4
\end{align*}$$

(where L = Lewis acid and E = ethyl formate)

Thus antimony(V) chloride is the strongest acceptor for ethyl formate, which has also been indicated by the conductance of solutions of Lewis acids in ethyl formate. Adducts of Lewis acids with ethyl chloroformate

The strong Lewis acids cause dehydroxylation of ethyl chloroformate and its mixtures with weak Lewis acids like arsenic(III) chloride and bromide, antimony(III) chloride
and bromide could only be examined spectroscopically. These studies do not indicate any significant perturbation in the spectral frequencies of ethyl chloroformate. The conductance measurements of the solutions of these Lewis acids in ethyl chloroformate, however, (as described earlier) indicate the formation of the addition compounds. Infrared spectral studies carried out by adsorbing ethyl chloroformate on aluminium chloride (91) have revealed that the carbonyl oxygen of ethyl chloroformate acts as a donor to aluminium chloride. On the basis of these findings, the interaction of weak Lewis acids resulting in the formation of addition compounds with ethyl chloroformate may be represented as:

\[ L + Cl - C \xrightarrow{\text{O}} Cl - C \xrightarrow{\text{O}} L \]  

\[ \text{O- Et} \quad \text{O- Et} \]  

\[ \cdots \text{(xxiii)} \]

On the basis of conductance studies (described earlier), the addition compound has been found to be fairly ionic. Keeping in view the above possible structure of the adduct and the ability of the chlorine atom to exist as \( Cl^- \) as indicated earlier, the adduct may be assigned the following mode of ionisation:

\[ L \xrightarrow{\text{O}} \]  

\[ \text{Cl- C- O- Et} \xrightarrow{\text{L Cl}} (L Cl) + (COO Et)^+ \]  

\[ \cdots \cdots \cdots \text{(xxiv)} \]
which supports the mode of ionisation of ethyl chloroformate as represented by equation (vii).

Adducts of tertiary organic bases with ethyl formate

The formation of addition compounds of tertiary organic bases like pyridine, quinoline, piperidine and \( \alpha \)-picoline with ethyl formate has already been indicated with the help of conductometric measurements. The addition compounds however could not be isolated. To further elucidate the mode of interaction of these bases with ethyl formate, infrared spectral studies of 1:1 molar mixtures of these bases with ethyl formate have been carried out.

Table XI presents a detailed record of the absorption frequencies of these bases alongwith those of their 1:1 molar mixtures with ethyl formate.

As is clear from Table XI, the infrared spectral frequencies of both ethyl formate and tertiary organic bases undergo perturbation on mixing. This may be explained as due to the interaction of tertiary organic bases with ethyl formate.

The highly electronegative character of carbonyl oxygen of ethyl formate may cause the development of a positive charge on the carbonyl carbon atom, which may be transferred to a hydrogen atom of ethyl group, through the hereal oxygen.

The fact that on complex formation with Lewis acids, the stretching frequency of \((\text{CO-0})\) group of ethyl formate
Table XI: Spectral frequencies of nitrogen organic bases and their adducts with ethyl formate

<table>
<thead>
<tr>
<th>Base</th>
<th>Assignment</th>
<th>$\nu$ (cm$^{-1}$)</th>
<th>$\nu$ (cm$^{-1}$)</th>
<th>$\nu$ (cm$^{-1}$)</th>
<th>$\nu$ (cm$^{-1}$)</th>
<th>$\nu$ (cm$^{-1}$)</th>
<th>$\nu$ (cm$^{-1}$)</th>
<th>$\nu$ (cm$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>Pyridine</td>
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<td>$\alpha$-picoline</td>
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<tr>
<td>Quinoline</td>
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<tr>
<td>Quinoline Piperidine</td>
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<tr>
<td>Piperidine</td>
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<tr>
<td>C-H</td>
<td>3020 s.</td>
<td>3020 s.</td>
<td>3020 s.</td>
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<td>2975 s.</td>
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<td>2925 v.</td>
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<td>2200 v.</td>
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<td>1930 s.</td>
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<td>1850 v.</td>
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<td>1780 m.</td>
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<td>1670 v.s.</td>
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<td>1670 v.s.</td>
<td>1670 v.s.</td>
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<td>1670 v.s.</td>
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<tr>
<td>1583 (C=O)</td>
<td>1583 (C=O)</td>
<td>1583 (C=O)</td>
<td>1583 (C=O)</td>
<td>1583 (C=O)</td>
<td>1583 (C=O)</td>
<td>1583 (C=O)</td>
<td>1583 (C=O)</td>
<td>1583 (C=O)</td>
</tr>
<tr>
<td>Pyridine</td>
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</tr>
<tr>
<td>$\nu$(C=O)</td>
<td>1320 w.</td>
<td>1320 w.</td>
<td>1320 w.</td>
<td>1320 w.</td>
<td>1320 w.</td>
<td>1320 w.</td>
<td>1320 w.</td>
<td>1320 w.</td>
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<tr>
<td>1375 s.</td>
<td>1375 s.</td>
<td>1375 s.</td>
<td>1375 s.</td>
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<tr>
<td>1300 s.</td>
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<td>1300 s.</td>
<td>1300 s.</td>
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<td>1215 m.</td>
<td>1215 m.</td>
<td>1215 m.</td>
<td>1215 m.</td>
<td>1215 m.</td>
<td>1215 m.</td>
<td>1215 m.</td>
<td>1215 m.</td>
<td>1215 m.</td>
</tr>
</tbody>
</table>

N.B. 1. The assignments of absorption frequencies of bases is based upon the results of Wilsheest and Burnstien (93) and of Cook and Church (94).

2. Refer to Table X for spectral frequencies of ethyl formate.
increases, favours the expected development of a positive charge on carbon or hydrogen atom of ethyl group.

The interaction of organic bases with ethyl formate may involve donation of electrons from the nitrogen atom of the base to one of the carbon or hydrogen atoms of ethyl group, resulting in the formation of quaternary ammonium (—N⁺) structure. This mode of interaction may lead to a decrease of (C—H) stretching frequency, increase of ν(C — O — C) while the carbonyl stretching frequency may be decreased:

\[
\begin{align*}
\text{H} & \quad \text{C} \\
\circlearrowright & \quad \text{C}_2\text{H}_5 \quad \text{N}
\end{align*}
\]

In the case of pyridine adduct with ethyl formate a medium intensity band is observed at 1730 cm⁻¹ which may be assigned to ν(C — O) group in the adduct. The band at 1190 cm⁻¹ due to (CO — O) group in ethyl formate shifts to a higher spectral region (1205 cm⁻¹) in the spectrum of the adduct.

The changes observed in the spectrum of pyridine in 1:1 mixture with ethyl formate are as follows:

1) The (C — H) stretching frequency at 3000 cm⁻¹ in pyridine shifts to the lower spectral region of 2925–2850 cm⁻¹.
11) The bands at 1583, 1570, 1483 and 1440 cm\(^{-1}\) due to C-C and C-N groups in pyridine shift to slightly higher regions at 1505, 1500, 1450 and 1450 cm\(^{-1}\) respectively.

Because of the very weak acidic character of ethyl formate, the spectral shifts observed in the spectrum of mixture of pyridine with ethyl formate are not as pronounced as may be expected of the ionic structure PyH\(^+\)/Cl\(^-\) (92) formed as a result of combination with a strong acid, but the donation of electrons by the nitrogen atom of pyridine is definitely indicated.

The spectra of 1:1 mixtures of ethyl formate with \(\alpha\)-picoline and quinoline (Table XI) reveal changes similar to those observed in the case of pyridine-ethyl formate adduct and thus support the proposed mode of interaction of bases with ethyl formate.

However, the spectrum of piperidine and ethyl formate adduct exhibits very strong bands in the spectral region of 3230-2660 cm\(^{-1}\) (characteristic of NH\(^+\) stretching frequency) (loc cit) which definitely justifies the donor character of nitrogen atom to the ethyl group (carbon or hydrogen) of ethyl formate. This frequency may also be assigned to the vibrational modes of N-H, where nitrogen atom of the base donates to the hydrogen atom of ethyl group.
of ethyl formate. Thus the structural representation in the limiting condition, of the interaction of bases with ethyl formate may be shown as:

\[
\begin{align*}
\text{H} - \text{C} - \text{O}_2\text{H}_5 + \text{B(base)} & \rightarrow \text{H} - \text{C} - \text{O}_2\text{H}_5 \\
& \uparrow \text{B} \\
(\text{HCOOH}_2\text{H}_4)^{-} + \text{BH}^{+} & \ldots(\text{xxv})
\end{align*}
\]

A similar situation has also been indicated by the spectral investigation carried out on the adducts of acetic anhydride with tertiary organic bases (95).

It implies, therefore, that the interaction of bases with ethyl formate, involves the association of the protons of ethyl formate with the base molecules and consequently this may be explained by assigning the mode of ionisation to ethyl formate as represented by equations (iii, iv and v).

Thus the infrared spectral studies support the results of electrochemical studies (described earlier) in ethyl formate.

**Adducts of tertiary organic bases with ethyl chloroformate**

In the preceding sections it has been pointed out that the organic nitrogen bases react with ethyl chloroformate to form addition compounds. Conductance studies of some of the bases in ethyl chloroformate have indicated that the addition
compounds are fairly ionic in nature and the higher conductance of the system has been ascribed to the existence of the ionic equilibria as represented by equation (vi)

In order to throw some light on the structure of the addition compounds of tertiary organic bases with ethyl chloroformate, the infrared spectral studies have been carried out. The spectral changes observed in the spectrum of ethyl chloroformate on complexing with nitrogen bases point out to a characteristic mode of interaction of bases with ethyl chloroformate. Table XII presents a record of spectral frequencies of ethyl chloroformate and its adducts with bases, \&

\alpha-picoline, quinoline, isoquinoline and piperidine.

The spectrum of ethyl chloroformate shows a strong band at 1780 cm\(^{-1}\) which may be ascribed to the carbonyl stretching frequency (87). The broad band at 1140-1200 cm\(^{-1}\) may be assigned for the stretching modes of vibrations due to (C-0-C) group whereas a strong band observed at 692 cm\(^{-1}\) may be due to the stretching mode of vibration of (C-Cl) group.

The absorption frequencies observed in the spectrum of ethyl chloroformate undergo appreciable perturbation on complex formation with the tertiary organic bases. The principal features of the spectral changes observed in the spectrum of ethyl chloroformate may be summed up as follows:

1) The carbonyl stretching frequency observed at 1780 cm\(^{-1}\) in the spectrum of ethyl chloroformate shifts to the lower spectral region of 1700-1635 cm\(^{-1}\) which may be thought to correspond to \(\nu(C=O)\) group.
Table XII: Major infrared spectral frequencies (cm⁻¹) of the nitrogen organic bases, ethyl chloroformate and their respective adducts

<table>
<thead>
<tr>
<th></th>
<th>Ethyl chloroformate</th>
<th>α-picoline (E. α-P)</th>
<th>Quinoline (Q. E.)</th>
<th>Isoquinoline (I. E.)</th>
<th>Piperidine (Pip. E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>v(cm⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3290 s, ν(N-H)</td>
<td>3150 s.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2925 m.</td>
<td>2977</td>
<td></td>
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<td></td>
<td>2840 m.</td>
<td>2775 m.</td>
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<tr>
<td></td>
<td>2600</td>
<td>2600</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(NH⁺)</td>
<td>2800 p.</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>1780</td>
<td>ν(C=O)</td>
<td>1650 c.s.</td>
<td>1655 v.s.</td>
<td>1635 s.</td>
<td>1700 m.</td>
</tr>
<tr>
<td></td>
<td>1890 m.</td>
<td>1630 s.</td>
<td>1602</td>
<td>1640 s.</td>
<td>1625 m.</td>
</tr>
<tr>
<td></td>
<td>1660 s.</td>
<td>1580 s.</td>
<td>1680 s.</td>
<td>1615 s.</td>
<td>1620 m.</td>
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<tr>
<td></td>
<td>1478 s.</td>
<td>1495 s.</td>
<td>1480 s.</td>
<td>1560 s.</td>
<td>1500 s.</td>
</tr>
<tr>
<td>(C-C)</td>
<td>1490 s.</td>
<td>1480 s.</td>
<td>1560 s.</td>
<td>1585 v.s.</td>
<td>1470</td>
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<tr>
<td>(C-N)</td>
<td>1508</td>
<td>1455</td>
<td>1340 s.</td>
<td>1390 m.</td>
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</tr>
<tr>
<td></td>
<td>1330 s.</td>
<td>1355 m.</td>
<td>1320 s.</td>
<td></td>
<td></td>
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</table>

Table continued on next page
Table XII continued

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
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<th>7</th>
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<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>1140-1200 γ(C=O-C)</td>
<td>1240 m.</td>
<td>1305 s.</td>
<td>1310 m.</td>
<td>(C=O-C) 1274</td>
<td>(C=O-C) 1274</td>
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<tr>
<td></td>
<td>1300 m.</td>
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<tr>
<td></td>
<td>1150 m.</td>
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<td></td>
<td></td>
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<td></td>
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<tr>
<td>(C=N)</td>
<td>998 m.</td>
<td>1050 s.</td>
<td>1005 m.</td>
<td>1030 s.</td>
<td>1010 m.</td>
<td>1035 s.</td>
<td>1120</td>
<td>1160 s.</td>
<td>1090 s.</td>
</tr>
<tr>
<td>ring vib.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>940 ring vib.</td>
<td></td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>860 m.</td>
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<td></td>
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<tr>
<td>692</td>
<td>(C-Cl)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>822 (H-N=C) 870 s.</td>
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<td></td>
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<tr>
<td></td>
<td>580</td>
<td>605 m.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>580</td>
<td>605 m.</td>
<td></td>
</tr>
</tbody>
</table>

* signifies new frequencies
- signifies absence.
11) The stretching frequency at 1140-1200 cm\(^{-1}\) assigned to \(\nu(C–O–C)\) in ethyl chloroformate, shifts to the higher spectral region of 1240-1310 cm\(^{-1}\) which may be assigned to \(\nu(C=O–C)\) group. These spectral changes are quite similar to the changes accompanying the spectra of the adducts of acetic anhydride with tertiary organic bases (95).

iii) The stretching frequency of 692 cm\(^{-1}\) which is assigned for \((C–Cl)\) group in ethyl chloroformate is absent in the spectra of the adducts. This situation is parallel to the absence of \(\nu(N–Cl)\) in the spectra of the adducts of nitrosyl chloride with tertiary amines (96). Since during the formation of complexes of ethyl chloroformate with nitrogen organic bases, there is no evolution of hydrochloric acid gas, it implies that the chlorine atom detached due to the cleavage of \((C–Cl)\) bond may be present as chloride ion in these complexes.

The changes observed in the spectrum of ethyl chloroformate on complex formation with tertiary organic bases are also similar to those observed in the spectrum of ethyl chloroformate adsorbed on aluminium chloride (91) where the lowering of carbonyl stretching frequency and an increase of \((C–O–C)\) have been assigned to the donor behaviour of carbonyl oxygen towards aluminium chloride. However, there is no indication of the formation of \((AlCl₄)\)\(^-\) ion.

In view of the structure of ethyl chloroformate \(\text{Cl}_2\text{C–O–Et}\), the highly electronegative character of chlorine
and the carbonyl oxygen, may cause the development of a positive charge on the carbonyl carbon. Consequently the interaction of nitrogen bases with ethyl chloroformate may be visualised as through the donation of the lone pair of electrons present on the nitrogen atom of the organic bases to the carbon atom in ethyl chloroformate. This mode of interaction may thus explain the changes observed in the spectrum of ethyl chloroformate on complexing with the nitrogen bases.

Because of the donor behaviour of the tertiary amines, the changes are also observed in the absorption frequencies of the bases. The major changes observed in the spectra of the bases as compared with the spectra of the adducts are as follows:

The significant absorption bands for C-O and C-N groups which occur at 1475-1625 cm\(^{-1}\), in the spectrum of tertiary amines, shift to the higher spectral region of 1495-1640 cm\(^{-1}\), in the spectra of the adducts of these amines with ethyl chloroformate. The extent of the shift observed in the frequencies of these groups is nearly the same as observed in the spectra of addition compounds of tertiary amines with very strong acceptors (92, 97, 98), wherein a bond is shown to be formed between the nitrogen of the bases and acceptor molecules.
It is worthwhile to point out that these changes are very nearly the same as observed when pyridine changes to pyridine - HCl adduct (PyH⁺Cl⁻) (92).

A new band is also observed in the spectral region of 1135-1176 cm⁻¹ and this has been ascribed to the vibration modes of (C=N) group and this implies that a strong bond is formed between the nitrogen of the bases and the carbonyl carbon of ethyl chloroformate.

The perturbations experienced by the frequencies of piperidine on complexing with ethyl chloroformate are more pronounced and substantiate the above mode of interaction of tertiary amines with ethyl chloroformate.

The (N-H) stretching frequency observed in the spectrum of piperidine at 3295 cm⁻¹ shifts to the lower spectral region of 3150 cm⁻¹. The H-C-C wagging and H-N-C deformation, and H-C-H bending frequencies are found to shift to the higher spectral region in the complex of piperidine with ethyl chloroformate. Similar shifts in the absorption frequencies of piperidine have also been reported by Greenwood and Wade (92) in the spectra of its adducts with a number of acceptors.

The decrease in the (N-H) stretching frequency of piperidine on formation of a complex with ethyl chloroformate may be attributed to the donation of non-bonding pair of electrons of the nitrogen atom, which consequently results in the weakening of (N-H) bond.
From the above observations it may be inferred that on complex formation with a base the chlorine atom of ethyl chloroformate is displaced by base molecule and the mode of interaction may be represented as:

\[
\begin{align*}
B(\text{base}) + \text{Cl} &\rightarrow \text{O} \\
\text{O} - \text{Et} &\rightarrow \left\{ B \text{C} \rightarrow \text{O} \right\} + \text{Cl}^- \\
&\text{...(xxvi)}
\end{align*}
\]

This structure also explains the formation of a new (C-N) bond in these complexes. Confirmation of the above structure is also provided by treating the addition compound of α-picoline and ethyl chloroformate with aluminium(III) and titanium(IV) chlorides, when addition products of the composition \((B,\text{ClCOOEt})\text{AlCl}_3\) and \((B,\text{ClCOOEt})_2\text{TiCl}_4\) respectively are obtained. Apart from the bands mentioned above, the infrared spectra of these complexes show additional bands at 660-570 cm\(^{-1}\) (b. s.) and 450-470 cm\(^{-1}\) (b. s.) respectively which may be assigned to the vibration of \((\text{AlCl}_4)^-\) ions (100) and the complexes may be represented as \((B,\text{ClCOOEt})^+\text{AlCl}_4^-\) and \((B,\text{ClCOOEt})^+\text{TiCl}_4^-\) respectively.

Thus the infrared spectral studies carried out with the adducts of ethyl chloroformate with nitrogen organic bases lead to the conclusion that the chlorine atom of ethyl chloroformate is capable of acquiring a negative charge i.e. Cl\(^-\) ionic character, which thus substantiates the ionisation of ethyl chloroformate which has been described earlier (equation vii).
SOLVOLYTIC REACTIONS

Solvolytic reactions have been carried out to synthesise different organic and inorganic compounds in various polar solvents and these reactions throw some light on the mode of autoionisation of the solvent. These reactions are viewed as exchange reactions between the ions of the solute and those of the solvent. If the solute dissolved in the solvent reacts with it in such a way that the concentration of the anions of the solvent changes, it is said to have undergone solvolysis of which hydrolysis occurring in water is a particular case.

A large number of solvolytic reactions have already been reported in acetyl chloride (101), benzoyl chloride (102) and acetic anhydride (103) and throw light on their modes of auto-ionisation. The utility of solvolytic reactions in acylhalides lies in the production of various anhydrous chlorides (loc cit) whereas anhydrous acetates and double acetates are obtained by carrying out the solvolytic reactions in acetic anhydride (loc cit). The Lewis acids like tin(IV) chloride and antimony(V) chloride have been solvolyzed in ethyl acetate by Paul and Malhotra (33) and the corresponding chloroethoxides have been obtained. The formation of the ethoxides has been explained on the basis of the presence of low concentration of ethoxide \((\text{OC}_2\text{H}_5)^-\) ions in ethyl acetate, which is assumed to ionise as:

\[
\text{CH}_3\text{COOC}_2\text{H}_5 \rightleftharpoons (\text{CH}_3\text{CO})^+ + (\text{OC}_2\text{H}_5)^- \quad \ldots \ldots (\text{xxvii})
\]
Solvolytic reactions have also been carried out in liquid ammonia and these reactions (known as ammonolysis) have indicated the existence of amide ions in liquid ammonia and have supported its autoionisation as:

\[ 2\text{NH}_3 \rightarrow \text{NH}_4^+ + \text{NH}_2^- \]  

\[ \text{(xxviii)} \]

Solvolytic reactions in liquid ammonia (104) bromine trifluoride (105), iodine pentafluoride (106), iodine monochloride (107), sulphur dioxide (108) and sulphuric acid (loc cit) have been successfully carried out and all these reactions have been found to be the exchange reactions between the ions of the solute and those of the solvent.

**Ethyl formate**

In order to lend support to the auto-ionisation of ethyl formate, solvolytic reactions of some metal halides have been carried out in it and the results of these reactions are being presented in this chapter.

Aluminium(III) chloride and bromide dissolve in ethyl formate in an exothermic reaction leading to the formation of monosolvates, which have been isolated and described in the preceding sections. However, on refluxing these Lewis acids with excess of ethyl formate they undergo solvolysis. The solvolyzed products on analysis have been found to correspond to the compositions as:

\[ \text{AlCl}(\text{HCOOC}_2\text{H}_4)_2 \] and \[ \text{AlBr}_2(\text{HCOOC}_2\text{H}_4) \]
The compound AICl\(_{(\text{HCOOC}_2\text{H}_4)_2}\) is a white crystalline solid, insoluble in nitrobenzene (decomp. 200\(^\circ\)C). The solvolysed product obtained from aluminium(III) bromide is a light brown crystalline substance (decomp. 200\(^\circ\)C). The gases liberated during the solvolysis of aluminium chloride and bromide are found to be hydrogen chloride and hydrogen bromide respectively, which on quantitative measurements, agree with the reactions given below:

\[
\begin{align*}
\text{AICl}_3 + 2\text{HCOOC}_2\text{H}_4 &= \text{AICl}(\text{HCOOC}_2\text{H}_4)_2 + 2\text{HCl} \uparrow \quad (xxix) \\
\text{AlBr}_3 + \text{HCOOC}_2\text{H}_4 &= \text{AlBr}(\text{HCOOC}_2\text{H}_4)_2 + \text{HBr} \uparrow \quad (xxx)
\end{align*}
\]

When iron(III) chloride is solvolysed with ethyl formate for about 18-24 hours, a reddish brown liquid compound FeCl(\text{HCOOC}_2\text{H}_4)_2 is obtained. The hydrogen chloride gas evolved during the course of the reaction agrees with the quantity required by the equation:

\[
\text{FeCl}_3 + 2\text{HCOOC}_2\text{H}_4 \rightarrow \text{FeCl}(\text{HCOOC}_2\text{H}_4)_2 + 2\text{HCl} \quad (xxxi)
\]

Tin(IV) and titanium(IV) chlorides react exothermally with the ethyl formate to give the disolvates. The formation of these solvates, may be explained on the basis of the hexacoordination of tin and titanium. However, on refluxing tin and titanium(IV) chlorides with ethyl formate the compounds SnCl\(_2(\text{HCOOC}_2\text{H}_4)_2\) (colourless liquid) and TiCl\(_2(\text{HCOOC}_2\text{H}_4)_2\) (light yellow viscous liquid) are formed. On the basis of analytical results, the solvolysed product and on the basis of
quantitative measurement of the hydrogen chloride liberated, the course of solvolytic reaction may be represented as:

\[ 
\text{MCl}_4 + 2\text{HCC} \xrightarrow{\text{HCOOC}} \text{MCl}_2(\text{HCOOC})_2 + 2\text{HCl} \uparrow \quad \text{...(xxxii)} 
\]

(where M stands for tin or titanium)

Under ordinary conditions, antimony(V) chloride forms a monosolvate with ethyl formate. On refluxing with excess of the solvent for about 1p-18 hours, however, a yellow coloured liquid of the composition \(\text{SbCl}_3(\text{HCOOC})_2\) separates out. During the course of solvolysis, hydrochloric acid gas is liberated which on estimation agrees with the proposed composition of the solvolysed product left behind. The overall reaction, representing the solvolysis of antimony(V) chloride may be represented as:

\[ 
\text{SbCl}_5 + 2\text{HCC} \xrightarrow{\text{HCOOC}} \text{SbCl}_3(\text{HCOOC})_2 + 2\text{HCl} \uparrow \quad \text{...(xxxiii)} 
\]

The period of refluxing required to bring about the solvolytic reactions and the partial replacement of the halogen atoms, further indicates that ethyl formate is weakly polar in nature, which is also indicated by its low conductance \((3 \times 10^{-7} \text{ ohm}^{-1} \text{cm}^{-1} \text{ at } 26^\circ) \) (40).

From the molecular formulae of the compounds listed in Table XIII, it appears that the elimination of hydrogen chloride or bromide during the course of solvolysis may lead to the formation of a metal carbon bond. The infrared spectra of
Table XIII: Compounds obtained by solvolysis

<table>
<thead>
<tr>
<th>Lewis acid</th>
<th>Solvolysed product</th>
<th>Physical state</th>
<th>m.p. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl₃</td>
<td>AlCl(HCOOC₂H₄)₂</td>
<td>White solid</td>
<td>700 (d)</td>
</tr>
<tr>
<td>AlBr₃</td>
<td>AlBr₂(HCOOC₂H₄)</td>
<td>Light brown solid</td>
<td></td>
</tr>
<tr>
<td>FeCl₃</td>
<td>FeCl(HCOOC₂H₄)₂</td>
<td>Reddish brown liquid</td>
<td>-</td>
</tr>
<tr>
<td>SnCl₄</td>
<td>SnCl₂(HCOOC₂H₄)₂</td>
<td>Colourless liquid</td>
<td>-</td>
</tr>
<tr>
<td>TiCl₄</td>
<td>TiCl₂(HCOOC₂H₄)₂</td>
<td>Light yellow viscous</td>
<td>-</td>
</tr>
<tr>
<td>SbCl₅</td>
<td>SbCl₃(HCOOC₂H₄)₂</td>
<td>Colourless liquid</td>
<td>-</td>
</tr>
</tbody>
</table>

The compounds SnCl₂(HCOOC₂H₄)₂ and SbCl₃(HCOOC₂H₄)₂ have indicated bands of medium intensity in the spectral region of 530 cm⁻¹ and 564 cm⁻¹ respectively, which are characteristic of (Sn–C) (109) and (Sb–C) bonds (110) which further support the structure of the major products of solvolysis as described above.

Thus it is found that in all these solvolytic reactions, replacement of the chloride ion with the anion (HCOOC₂H₄)⁻ takes place which suggests the possible existence of (HCOOC₂H₄)⁻ ion in ethyl formate and lends further support to the mode of ionisation of ethyl formate (equation iii).
Ethyl chloroformate

As the strong Lewis acids are found to cause
decarboxylation of ethyl formate (65-67), their solvolytic
reactions could not be carried out.
Conductometric titrations in ethyl formate

Acid-base neutralisation reactions have been studied in various protonic and non-protonic solvents and conductance measurements constitute a convenient method for the detection of equivalence point. Conductometric titrations have been carried out in liquid sulphur dioxide (111), nitrosyl chloride (112), acetyl chloride (113), benzoyl chloride (114), phosphoryl chloride (115), thionyl bromide (g8), phosphoryl bromide (g8) and ethyl acetate (30) and the existence of acidic and basic species in these solvents has been indicated. Acid-base neutralisation reaction between tin(IV) chloride and nitrogen organic bases (B) in acetyl chloride has been explained by Paul et al (loc cit) as follows:

\[
\text{SnCl}_4 + 2\text{CH}_3\text{COCl} \rightarrow \text{SnCl}_4\cdot 2\text{CH}_3\text{COCl} \rightleftharpoons (\text{SnCl}_6)^{2-} + 2(\text{CH}_3\text{CO})^+
\]

(formation and ionisation of solvo acid) \hspace{1cm} \text{(...) (xxxiv)}

\[
2\text{B} + 2\text{CH}_3\text{COCl} \rightarrow 2\text{B}\cdot (\text{CH}_3\text{COCl})_2 \rightleftharpoons 2(\text{B}\cdot \text{CH}_3\text{CO})^+ + 2\text{Cl}^-
\]

(formation and ionisation of solvo base) \hspace{1cm} \text{(...) (xxxv)}

\[
2(\text{B}\cdot \text{CH}_3\text{CO})^+ + 2\text{Cl}^-\cdot (\text{SnCl}_6)^{2-} \rightarrow 2(\text{CH}_3\text{CO})^+ + 2(\text{CH}_3\text{CO})^+
\]

(\text{B}\cdot \text{CH}_3\text{CO})_2\text{SnCl}_6 + 2\text{CH}_3\text{COCl} \hspace{1cm} \text{(...) (xxxvi)}

(neutralisation reaction)
In the preceding pages the auto-ionisation of ethyl formate has been represented by equation (iii).

According to the definition of acids and bases, a solute which on dissolution in ethyl formate increases directly or indirectly, the concentration of $H^+$ ions will behave as an acid, whereas the one which increases the concentration of \((\text{HCOOC}_2\text{H}_4)^-\) anions, characteristic of the solvent, acts as a base. Thus the protonic acids and Lewis acids should behave as ansolvo and solvo acids respectively. The tertiary organic bases which react with ethyl formate forming the addition compounds which on ionisation, produce the anions characteristic of the solvent are likely to behave as solvo bases. In order to confirm that the proposed acidic and basic species are real, their neutralisation reactions have been studied conductometrically and potentiometrically in ethyl formate.

**Lewis acid-base systems**

Since most of the Lewis acids and bases readily dissolve in ethyl formate, giving fairly conducting solutions, the neutralisation reactions between the Lewis acids, antimony(V) chloride, tin(IV) chloride and tin(IV) bromide and the nitrogen organic bases pyridine, quinoline, $\alpha$-picoline and diethyl aniline have been studied conductometrically.

Antimony(V) chloride has already been used as an acidic titrant for estimating bases in acetyl chloride, benzoyl
chloride and nitrosyl chloride (loc. cit.). In all these solvents the monobasic character of antimony(V)chloride has been established on the basis of its acquiring a stable hexa coordination.

As has been indicated in the preceding sections, antimony(V)chloride forms a mono-solvate with ethyl formate which may be proposed to ionise as per equation (x).

The organic bases quinoline, pyridine, α-picoline and diethyl aniline have been titrated against a solution of antimony(V)chloride in ethyl formate. The relative conductance of the resulting solution is plotted against the composition as represented by the molar ratio of acid/base (Fig.12). The conductance of the solution goes on increasing with the addition of antimony(V)chloride solution, till at the 1:1 molar ratio of acid/base a sharp break in the conductance curve is observed which indicates the formation of the neutralisation complex. The increase in conductance may be explained by the solubility of the neutralisation complex in ethyl formate. In view of the proposed auto-ionisation of ethyl formate the neutralisation reaction could be explained by the following reactions:

\[
\text{SbCl}_5 + \text{HCOOC}_2\text{H}_5 \rightarrow \text{SbCl}_5\cdot\text{HCOOC}_2\text{H}_5 \rightleftharpoons \\
(\text{SbCl}_5\cdot\text{HCOOC}_2\text{H}_4)^+ + \text{H}^+ \\
\text{(formation of solvo acid)}
\]
CONDUCTOMETRIC TITRATIONS OF LEWIS ACIDS AGAINST BASES

FIG 2: ANTIMONY (V) CHLORIDE

VS QUINOLINE
PYRIDINE
α-PICOLINE
DIETHYLANILINE

FIG 3: TIN (IV) CHLORIDE

VS α-PICOLINE
PYRIDINE
DIETHYLANILINE
The tertiary organic bases have also been titrated conductometrically against the solution of tin(IV) chloride and the variation of conductance following the addition of tin(IV) chloride solution to the solution of bases in ethyl formate is graphically represented in Fig. 13. The conductance curves show two breaks at the acid/base molar ratio of 0.5:1 and 1:1. The break at the composition represented by the molar ratio of acid/base as 0.5:1, indicates the formation of the normal salt while the break at 1:1 molar ratio indicates the formation of the acid salt. This shows that tin(IV) chloride behaves as a dibasic solvo acid in ethyl formate and this is quite in agreement with the earlier findings. The increase in conductance, may be explained as due to the fair solubility of neutralisation complexes which could not be isolated.

In view of the proposed auto-ionisation of ethyl formate, the neutralisation reaction indicating the formation of normal and acid salts may be represented as

$$\text{SnCl}_4 + 2\text{HCOOC}_2\text{H}_5 \rightarrow \text{SnCl}_4\cdot 2\text{HCOOC}_2\text{H}_5 \rightleftharpoons \text{SnCl}_4\cdot 2\text{HCOOC}_2\text{H}_5 + 2\text{H}^+$$

(formulation & ionisation of solvo acid) ...(xxxviii)
\[ (\text{base}) + \text{HCOOC}_2\text{H}_5 \rightarrow \text{b.HCOOC}_2\text{H}_5 \rightarrow \text{BH}^+ + \text{HCOOC}_2\text{H}_4^- \]

(formation and ionisation of solvo base) .... (xxxviiia)

\[ (\text{SnCl}_4 + 2\text{HCOOC}_2\text{H}_4)^{2-} + 2\text{BH}^+ + 2\text{H}^+ + 2\text{HCOOC}_2\text{H}_4^- \rightarrow \]

\[ (\text{BH})_2^+ (\text{SnCl}_4 + 2\text{HCOOC}_2\text{H}_4)^{2-} + 2\text{HCOOC}_2\text{H}_5^- \]

(normal salt) ..... (xxxviiib)

**Formation of acid salt**

The normal salt further reacts with another solvated molecule of the Lewis acid, to give rise to the acid salt as shown below:

\[ (\text{BH})_2\text{SnCl}_4 + 2\text{HCOOC}_2\text{H}_4 + \text{SnCl}_4 + 2\text{HCOOC}_2\text{H}_4 \rightarrow \]

\[ 2(\text{BH}.\text{H}.\text{SnCl}_4 + 2\text{HCOOC}_2\text{H}_4) \] .... (xxxix)

(acid salt)

**Protonic acid-base systems**

Conductometric titrations between perchloric, p-toluene sulphuric, methane sulphuric, perfluorobutyric acids and tertiary organic bases in ethyl acetate have been carried out by Hall (116). Recently Paul et al have reported the conductometric titrations between the protonic acids and various organic bases in ethyl acetate (30), formamide (13) and in molten acetamide (12).

In the present work, conductometric titrations of fluorosulphuric, disulphuric and sulphuric acids have been
carried out against pyridine, quinoline, \(\alpha\)-picoline and diethylaniline in ethyl formate (Figs. 14-16).

Fluorosulphuric acid forms a monosolvate with ethyl formate which has been proposed to ionise as:

\[
FSO_3H \cdot HCOOC_2H_5 \rightleftharpoons (HCOOC_2H_5 \cdot H)^+ + (SO_3F^-) \quad \ldots \ldots (x I)
\]

The neutralisation reaction between fluorosulphuric acid and the tertiary organic bases has been studied by adding the acidic solution to the solution of the bases in ethyl formate and noting the conductance of the resulting solution and the plots of conductance against the composition as represented by acid/base molar ratio are presented in Fig. 14. The conductance of the solution goes on increasing regularly, till at the molar ratio acid/base of 1:1, a sharp break in the curve is observed. This indicates the formation of the neutralisation complex of the indicated composition. Beyond this point, the conductance curve becomes less steep. No solid complexes could be isolated because of their solubility in ethyl formate.

In view of the proposed auto-ionisation of ethyl formate, the neutralisation reactions may be explained as follows:

\[
FSO_3H + HCOOC_2H_5 \rightarrow FSO_3H \cdot HCOOC_2H_5 \rightleftharpoons (HCOOC_2H_5 \cdot H)^+ + SO_3F^-
\]

(ionisation of ansolvo acid) \ldots \ldots (x I I)
CODUCTOMETRIC TITRATIONS IN ETHYL FORMATE

FIG. 15 DISULPHURIC ACID

- QUINOLINE
- PYRIDINE
- α-PICOLINE
- DIETHYLAMINE

FIG. 14 FLUOROSULPHURIC ACID

- PYRIDINE
- α-PICOLINE
- DIETHYLAMINE
- QUINOLINE

RELATIVE CONDUCTANCE x 10^6

MOLAR RATIO ACID/BASE

MOLAR RATIO ACID/BASE
The use of sulphuric acid as titrant in acetic acid (84,117), dimethyl formamide (118) and ethyl acetate (82) has already been reported. It has been described in the preceding sections, that sulphuric acid dissolves in ethyl formate in an exothermic reaction and the resulting solution is found to be fairly conducting.

The bases pyridine, quinoline, α-picoline and diethyl aniline have been titrated conductometrically against the solutions of sulphuric acid in ethyl formate and the results of these titrations are presented in Fig.16. The curves thus obtained show a break at the molar ratio of acid/base as 0.5:1, which indicates the formation of the normal salt. The course of the neutralisation reaction may be explained as follows:

\[
\begin{align*}
H_2SO_4 + 2HCOOC_2H_5 &\rightarrow H_2SO_4.2HCOOC_2H_5 \rightleftharpoons 2(H_2HCOOC_2H_5)^+ + SO_4^{2-} \\
&\quad \text{(formation and ionisation of an solvo acid) } \ldots \ldots \ldots \ldots \ldots \ldots (xli)
\end{align*}
\]

\[
\begin{align*}
2B + 2HCOOC_2H_5 &\rightarrow 2B,HCOOC_2H_5 \rightleftharpoons 2BH^+ + 2(HCOOC_2H_4)^- \\
&\quad \text{(formation and ionisation of solvo base) } \ldots \ldots \ldots \ldots \ldots \ldots (xliia)
\end{align*}
\]
FIG. 16 CONDUCTOMETRIC TITRATION OF SULPHURIC ACID

VS

PYRIDINE

α-PICOLINE

DIETHYLANILINE

QUINOLINE

RELATIVE CONDUCTANCE $\times 10^5$

0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5

MOLAR RATIO ACID/BASE
The result of the conductometric titration between disulphuric acid and the nitrogen organic bases are graphically represented by the Fig. 15 and the course of the neutralisation reaction can be explained on lines similar to those of fluorosulphuric and sulphuric acids.

Conductometric titrations in ethyl chloroformate

Ethyl chloroformate has been proposed to ionise as per equation (vii) in the preceding section.

The weak Lewis acids like antimony(III)chloride, antimony(III)bromide and arsenic (III)chloride react with ethyl chloroformate in such a way that the addition compounds formed, undergo ionisation and furnish the cations (COOC₂H₅)⁺ characteristic of the solvent. The interaction of the nitrogen organic bases leads to the formation of adducts which on ionisation produce the anions (Cl⁻) characteristic of the solvent. This is quite in agreement with the definition of acids and bases which are defined as the solutes producing the cations or the anions characteristic of the solvent respectively.

To confirm that the expected behaviour of the Lewis acids and bases in ethyl chloroformate is real, the conductometric
and potentiometric titrations have been carried out in ethyl chloroformate.

As has been described earlier, the acid-base neutralisation reactions have been carried out in many protonic and non-protonic solvents and consequently the existence of acidic and basic species has been indicated.

Since the Lewis acids antimony(III)chloride, antimony(III) bromide and arsenic(III)chloride and the bases dimethyl aniline and diethyl aniline produce fairly conducting solutions in ethyl chloroformate the neutralisation reactions have been studied conductometrically and the results obtained have been substantiated potentiometrically.

**Lewis acid-base systems**

It has been described in the preceding section, that arsenic(III)chloride forms a monosolvate with ethyl chloroformate and on the basis of its conductance it has been proposed to ionise as:

\[
(\text{AsCl}_2\cdot\text{ClCOOC}_2\text{H}_5) \rightleftharpoons (\text{AsCl}_2^- \ + \ (\text{COOC}_2\text{H}_5)^+)
\]  

\[
(\text{xliii})
\]

The nitrogen organic bases dimethyl and diethyl anilines have been titrated against the solution of the arsenic(III) chloride in ethyl chloroformate. The solution of arsenic(III) chloride in ethyl chloroformate has been added to the solution of the base in the conductivity cell and relative conductance
is noted. Plot of conductance against the composition as represented by the molar ratio of acid/base is presented in Fig. 17.

On the addition of the acid solution to the solution of the base, the conductance goes on increasing, till at the composition represented by the molar ratio of acid/base as 0.5:1, a sharp break in the curve is observed. Beyond this point the conductance remains almost constant. The initial increase in the conductance is explained as due to the ionic nature of the neutralisation complex which has a fair solubility. Keeping in view the ionisation of ethyl chloroformate as mentioned earlier, the neutralisation reaction may be explained as follows:

\[
\text{AsCl}_3 + \text{CICOOC}_2\text{H}_5 \rightarrow \text{AsCl}_3\cdot\text{CICOOC}_2\text{H}_5 \rightleftharpoons \text{AsCl}_4^- + (\text{CICOOC}_2\text{H}_5)^+ \\
\text{formation of solvo acid) .... (xliv)}
\]

\[
2\text{B(base)} + \text{CICOOC}_2\text{H}_5 \rightarrow 2(\text{B.CICOOC}_2\text{H}_5) \rightleftharpoons 2\text{Cl}^- + 2(\text{B.CICOOC}_2\text{H}_5)^+ \\
\text{formation of solvo base) .... (xliia) }
\]

\[
\text{AsCl}_4^- + (\text{CICOOC}_2\text{H}_5)^+ + 2\text{B.CICOOC}_2\text{H}_5^+ + \text{pCl}^- \rightarrow \\
(\text{B.CICOOC}_2\text{H}_5)_2\text{AsCl}_4 \text{ Cl} + \text{CICOOC}_2\text{H}_5 \\
\text{neutralisation reaction) .... (xlivb)}
\]

The neutralisation complexes, the formation of which is conductometrically indicated, have been isolated, washed with dry carbon tetrachloride and finally dried under vacuum. On
FIG. 17 CONDUCTOMETRIC TITRATION OF ARSENIC (III) CHLORIDE

VS

- - DIMETHYL ANILINE

△三角 DIETHYL NILINE

RELATIVE CONDUCTANCE X (10^{-5})

MOLAR RATIO ACID/BASE

0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3
analysis, they have been found to correspond to the composition represented by the formula $pB_{2}AsCl_{3}$. It may be assumed that the neutralisation complex gets desolvated during the process of drying, and thus the formation of $(pB_{2}AsCl_{3})$ may be explained as:

$$\left[(C_{2}H_{5}COO)_{2}AsCl_{2}\right]^{+}Cl^{-} \rightarrow 28AsCl_{3} + 2C_{2}H_{5}COOCl$$

Figure 18 describes the results of conductometric titration between the bases dimethyl and diethyl anilines and the solvo acid antimony(III)chloride. In the case of diethylaniline, the conductance of the solution of the base goes on increasing with the addition of Lewis acid solution, till a sharp break is observed at the composition represented by the molar ratio of acid/base as 1:1. At this point, precipitation takes place and the subsequent addition of the acid solution, only causes a slight decrease in the conductance. The initial increase in the conductance may be explained as due to the ionic nature of the neutralisation complex, which is soluble and the decrease in conductance beyond the molar ratio of 1:1 may be attributed to the dilution effect. The neutralisation complex has been actually isolated and analysed and is found to agree with the composition represented by the formula $(D_{2}A_{2}COO)_{2}SbCl_{4}$, indicating that the solvent molecules are not lost during the drying of the precipitate indicating possibly that $SbCl_{3}$ is a strong Lewis acid than $AsCl_{3}$. 

---
The curve representing the titration of dimethyl aniline against antimony(III)chloride shows two breaks which correspond to the formation of salts with acid/base molar ratios of 1:2 and 1:1 respectively (Fig. 18). It has been found that initially the conductance increases, with the addition of the acid solution to that of dimethyl aniline in ethyl chloroformate, but at the molar ratio of acid/base as 0.2:1, a precipitate appears. Further addition of the titrant does not result in any further increase in the conductance, but the precipitate goes on increasing in quantity. When the molar ratio of acid/base as 1:2 reached, further addition of the Lewis acid solution, results in the decrease of conductance and it continues to decrease till the molar ratio of acid/base as 1:1 is reached. Beyond this point the conductance again starts increasing and may be explained as due to the presence of the excess of the Lewis acid solution which is quite conducting. The initial increase in the conductance may be explained as due to the ionic nature of the normal salt. When the normal salt is completely precipitated, further addition of the acid solution results in the conversion of normal salt into the acid salt which is more insoluble, and thus explains the decrease in the conductance, till the normal salt is completely changed into the acid salt. After that any further addition of the acid titrant results in the increase of conductance of the solution.

The formation of the normal salt and the acid salt may be explained by the following reactions:

\[ \text{Normal Salt} \rightarrow \text{Acid Salt} \]

\[ \text{Lewis Acid} + \text{Normal Salt} \rightarrow \text{Acid Salt} + \text{Lewis Base} \]
FIG. 18 CONDUCTOMETRIC TITRATION OF ANTIMONY (III) CHLORIDE

VS

DIMETHYLANILINE

DIETHYLANILINE

RELATIVE CONDUCTANCE × 10^6

0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4

MOLAR RATIO ACID/BASE
Formation of normal salt

\[ \text{SbCl}_3 + 2\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5 \rightarrow \text{SbCl}_3.2\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5 \rightleftharpoons \text{SbCl}_3.2\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5 + \text{SbCl}_3 + 2\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5 \]

(formation of solvo acid) \( \cdots \) (xlvi)

\[ \text{SbCl}_5 + 2\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5 \rightarrow \text{SbCl}_5.2\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5 \rightleftharpoons \text{SbCl}_5.2\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5 + \text{SbCl}_3 + 2\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5 \]

(formation of solvo base) \( \cdots \) (xlvia)

\[ (\text{SbCl}_5)^2- + 2(\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5)^+ + 2\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5 + 2\text{Cl}^- \rightarrow \]

\[ \left[ \text{SbCl}_5.2(\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5) \right] + 2\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5 \]

(neutralisation) (normal salt) \( \cdots \) (xlvib)

\[ \left[ (\text{SbCl}_5).2(\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5) \right] \xrightarrow{\text{desolvation}} \text{SbCl}_3.2\text{C}_2\text{H}_5 \]

\( \cdots \) (xlvii)

Formation of acid salt

\[ \text{SbCl}_3 + 2\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5 \rightarrow \text{SbCl}_3.2\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5 \rightleftharpoons \text{SbCl}_3.2\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5 + \text{SbCl}_3 + 2\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5 \]

(formation of solvo acid) \( \cdots \) (xlviii)

\[ 3\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5 \rightarrow 3\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5 + \text{SbCl}_3 \]

(formation of solvo base) \( \cdots \) (xlviiia)

\[ (\text{SbCl}_5)^2- + 2(\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5)^+ + (\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5)^+ + \text{Cl}^- \rightarrow \]

\[ \left[ \text{SbCl}_5.2(\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5) \right] + 2\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5 \]

(neutralisation) \( \cdots \) (xlviiib)

\[ \left[ \text{SbCl}_5.2(\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5) \right] \xrightarrow{\text{desolvation}} \text{SbCl}_3.\text{C}_2\text{H}_5 \]

\( \cdots \) (xlix)
The neutralisation complex has actually been isolated, analysed and is found to agree with the formula \((\text{SbCl}_3\cdot\text{DEA})\) and is assumed to have been formed due to the desolvation of the neutralisation product.

The results of the conductometric titration of the bases dimethyl aniline and diethylaniline against antimony (III) bromide are presented in Fig. 19. The results seem to be quite in agreement with the titration of diethyl aniline against antimony(III) chloride and hence can be explained on similar lines. In this case the complexes which have been isolated agree with the formula \(\text{SbBr}_3\cdot\text{DMA}\) and \(\text{SbBr}_3\cdot\text{DEA}\). The neutralisation complexes isolated in ethyl chloroformate are listed in Table XIV.

**Table XIV: Neutralisation complexes in ethyl chloroformate**

<table>
<thead>
<tr>
<th>System</th>
<th>Titrant</th>
<th>Stoichiometric ratio indicated</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{AsCl}_3\cdot\text{Dimethylaniline})</td>
<td>(\text{AsCl}_3)</td>
<td>(\text{AsCl}_3\cdot\text{C}<em>6\text{H}</em>{5}\text{N}((\text{CH}_3)_2))</td>
</tr>
<tr>
<td>(\text{AsCl}_3\cdot\text{Diethylaniline})</td>
<td>(\text{AsCl}_3)</td>
<td>(\text{AsCl}_3\cdot\text{C}<em>6\text{H}</em>{5}\text{N}((\text{C}_2\text{H}_5)_2))</td>
</tr>
<tr>
<td>(\text{SbCl}_3\cdot\text{Diethylaniline})</td>
<td>(\text{SbCl}_3)</td>
<td>(\text{SbCl}_3\cdot\text{C}<em>6\text{H}</em>{5}\text{N}((\text{CH}_3)_2\text{}))</td>
</tr>
<tr>
<td>(\text{SbCl}<em>3\cdot\text{C}</em>{10}\text{H}_{16}\text{N}((\text{C}_2\text{H}_5)_2))</td>
<td>(\text{SbCl}_3)</td>
<td>(\text{SbCl}_3\cdot\text{C}<em>6\text{H}</em>{5}\text{N}((\text{C}_2\text{H}_5)_2))</td>
</tr>
<tr>
<td>(\text{SbBr}_3\cdot\text{Dimethylaniline})</td>
<td>(\text{SbBr}_3)</td>
<td>(\text{SbBr}_3\cdot\text{C}<em>6\text{H}</em>{5}\text{N}((\text{CH}_3)_2\text{}))</td>
</tr>
<tr>
<td>(\text{SbBr}_3\cdot\text{Diethylaniline})</td>
<td>(\text{SbBr}_3)</td>
<td>(\text{SbBr}_3\cdot\text{C}<em>6\text{H}</em>{5}\text{N}((\text{C}_2\text{H}_5)_2))</td>
</tr>
</tbody>
</table>
FIG. 19 CONDUCTOMETRIC TITRATION OF ANTIMONY(III) BROMIDE

VS

○○ DI ETHYLAMINE

△△ DIE HYLONILE

RELATIVE CONDUCTANCE \times 10^6

50
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12

0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4

MOLAR RATIO ACID/BASE
Protonic acid-base system

As the protonic acids are found to bring about the decomposition of ethyl chloroformate, the conductometric titrations between protonic acids and nitrogen organic bases could not be carried out.

Potentiometric titrations in ethyl formate

Quite often, the acid-base neutralisation reactions in a solvent, have been studied by means of potentiometric titrations. Organic amines and certain metallic acetates have been titrated electrometrically against strong inorganic acids in acetic acid (119). Neutralisation reactions between Lewis acids and tetramethyl ammonium chloride have been potentiometrically studied in benzoyle chloride (120). Recently Paul et al have carried out potentiometric titrations in molten acetic acid (12) to study the acid-base neutralisation reaction. It has been observed that the potential jumps near the end point are not comparable to those observed in water as a solvent, but still the results are quite encouraging.

Apart from studying the neutralisation reactions, potentiometric titrations have also helped in differentiating the strength of various protonic acids, isocyanates, and the tertiary organic bases in a particular solvent.
In addition to confirming the results of conductometric titrations, the potentiometric titrations may also indicate the formation of more complexes, by showing more inflexion points, than are indicated by the conductometric titrations.

Potentiometric titrations between protonic acids and organic bases have been carried out in dioxane, acetonitrile and ethyl acetate by Hall (loc cit) by using glass electrodes as the hydrogen ion indicator electrode and calomel electrode as the reference electrode. In the solvents like acetyl chloride (loc cit), acetic acid (loc cit), acetic anhydride (loc cit), formamide (loc cit) and dimethyl formamide, acid-base neutralisation reactions have been successfully studied by using fibre type calomel electrode. In ethyl formate potentiometric titrations have been carried out, using calomel as the reference electrode.

**Lewis acid-base systems**

The results of potentiometric titrations between Lewis acids and the tertiary organic bases in ethyl formate are graphically presented in the Figs. 20, 21 and 22.

Figure 20 shows the results of titration between antimony(V)chloride and the tertiary organic bases pyridine, α-picoline, quinoline and diethylaniline. Addition of acid solution to the solution of the base in ethyl formate causes the potential to increase gradually, till at the composition represented by the molar ratio of acid base as 1:1, a sudden jump in the e.m.f. is noticed which indicates the formation of
POTENTIOMETRIC TITRATIONS IN ETHY FORMATE

FIG. 21 TIN (IV) CHLORIDE

Vs QUINOLINE
DIETHYLANILINE
PYRIDINE
α-PICOLINE

480
460
440
420
400
380
360
340
320
300

e.m.f. (m.volls) (SnCl4)
0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6
— MOLAR RATIO ACID/BASE —

0 0.2 0.4 0.6 0.8 1.0 1.2 1.4
— MOLAR RATIO ACID/BASE —

FIG. 20 ANTI ONY (V) CHLORIDE

Vs PYRIDINE
α-PICOLINE
QUINOLINE
DIETHYLANILINE

600
580
560
540
520
500
480
460

e.m.f. (m.volls) (SbCl5)
FIG 22 POTENTIOMETRIC TITRATION OF TIN(IV) BROMIDE.

\[ \text{emf. (m. volts)} \]

\[ \begin{align*}
\text{e.m.f.} & \quad 0.1 \quad 0.2 \quad 0.3 \quad 0.4 \quad 0.5 \quad 0.6 \quad 0.7 \quad 0.8 \quad 0.9 \quad 1.0 \quad 1.2 \quad 1.3 \\
\text{MOLAR RATIO ACID BASE} & \end{align*} \]
It is a neutralisation complex between the acid and base. This shows that antimony(V) chloride behaves as a monobasic acid in ethyl formate and thus confirms the results of conductometric titration (described earlier).

Tin(IV) chloride and bromide have also been titrated potentiometrically against the tertiary organic bases and the results (shown by Fig. 21, 22) are found to be quite in agreement with the results obtained during the course of conductometric titrations.

Protonic acid-base system

Apart from using Lewis acids as titrants, the tertiary organic bases have also been titrated against fluorosulphuric, disulphuric and sulphuric acids. The results of these titrations are graphically represented by the Fig. 23, 24 and 25. The monobasic character of fluorosulphuric acid and disulphuric acid and dibasic character of sulphuric acid in ethyl formate is indicated by the potential jumps observed at 1:1 or 1:2 molar ratio of acid/base. As has been mentioned in the conductometric titrations, the mechanism of neutralisation reactions can be explained on the basis of the auto-ionisation of ethyl formate (equation iii).

Potentiometric titrations in ethyl chloroformate

The usefulness of the potentiometric titration in studying the acid-base neutralisation reactions in a particular solvent and in throwing light on the nature of ionic species in the solvent has already been described.
POTENTIOMETRIC TITRATIONS IN ETHYL FORMATE

**FIG. 23** FLUOROSULPHURIC ACID VS PYRIDINE
- PICYLINE
- QUINOLINE
- DIETHYLANILINE

**FIG. 24** DISULPHURIC ACID VS quinoline
- PICOLINE
- ICOLINE
- DIETHYL ANILINE
- PRIDINE

MOLAR RATIO ACID/BAS: 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5
MOLAR RATIO ACID/BASE: 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5
FIG 25 POTETIOMETRIC TITRATIONS N ETHYL
FORMATE SULPHURIC ACID

VS α-PICOLINE
PYRIDINE
DIETHYLANILINE
QUINOLINE

MOLAR RATIO ACID/BASE
Lewis acid-base system

In order to confirm the results of the conductometric titrations, acid-base neutralisation reactions have also been studied potentiometrically in ethyl chloroformate. The potentiometric titrations between the Lewis acids arsenic(III) chloride, antimony(III) chloride and bromide and the bases dimethylaniline and diethylaniline have been carried out, using the flat type calomel electrode as the reference electrode. The results of the potentiometric titrations have been graphically presented in the Figs. 26, 27 and 28.

The acidic solution has been added to the solution of the base and the e.m.f. measured has been plotted against the composition as represented by the molar ratio of acid/base.

The e.m.f. of the system goes on increasing gradually with the addition of the Lewis acid solution and at the molar ratio of acid/base as 0.5, a jump in the potential is observed which indicates the formation of the neutralisation complex. After this point the increase in potential is very slow. These results are quite in agreement with the findings described in the conductometric titrations. As has been mentioned in the conductometric titrations, the neutralisation reactions have been explained on the basis of the mechanism which assumes the auto-ionisation of ethyl chloroformate as represented by equation (vii).
FIG 26 POTENTIOMETRIC TITRATION (IN ETHYL CHLOROFORMATE) OF ARSENIC(III) CHLORIDE.

**Variation of** e.m.f. m. volts **vs molar ratio acid/base.**

- **Diethylaniline**
- **Dimethylaniline**
FIG 27 POTENTIOMETRIC TITRATION OF ANTIMONY (III) BROMIDE.

- **DIMETHYLANILINE**
- **DIETHYLANILINE**

MOLAR RATIO ACID/BASE

0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3

e.m.f. (m.vols.)
FIG. 28 POTENTIOMETRIC TITRATION IN ETHYL CHLOROFORMATE OF ANTIMON (III) CHLORIDE.

Vs

\( Q \cdot Q \) DIETHYLANILINE

\( \triangle \cdot \triangle \) DIMETHYLANILINE

MOLAR RATIO ACID/BASE

0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4