INTRODUCTION

Excellent solvent properties of water have actually hindered the development of chemistry in non-aqueous solvents and till recently, most of chemistry was developed only in aqueous solutions. However, reactions involving certain compounds which are susceptible to hydrolytic attack, could not be carried out in the presence of water. Attempts to solve this difficulty have been made by carrying out all such reactions in non-aqueous media and as a result, a large number of compounds have gained prominence as non-aqueous solvents.

Non polar solvents do not play any specific role except that of a diluent. Polar solvents which are of great interest for their influence on the course of reactions may be divided into protonic and non-protionic solvents. Among the compounds used as protic or protonic solvents, liquid ammonia (1,2), sulphuric acid (3,4), anhydrous hydrofluoric acid (5,6), methyl alcohol (7,8), acetic acid (9-11), molten acetamide (12), formamide (13), and dimethyl formamide (14) are worth mentioning. As in water, the acid-base reactions in these solvents have been considered to involve proton transfer.

Among the aprotic or non protonic solvents, mention may be made of dinitrogen tetraoxide (15) and liquid sulphur dioxide (16,17). The oxyhalides and halides like nitrosyl chloride (18,19)
phosphoryl chloride (f0,2), phosphoryl bromide (2,2), thionyl bromide (22), seleninyl chloride (23,24), iodine monochloride (25), acetyl chloride (26,27) and benzoyl chloride (28,29) have also been developed as non-aqueous solvents.

Most of the esters have convenient working range and are stable under ordinary conditions. They are largely being employed as industrial solvents. But the nature of various chemical reactions taking place in these esters and the other important aspects of their solvent chemistry, have not yet been studied in detail. However, recently, Paul and Malhotra (30-33) have carried out some work on ethyl acetate. Ethyl formate is closely related to ethyl acetate except that ethyl acetate is an ester of acetic acid while ethyl formate is an ester of formic acid. It is expected that some of the differences in the properties of the two acids may be reflected in the esters too. In view of the successful development of a large number of compounds as non-aqueous solvents in general and that of ethyl acetate in particular, the present work has been undertaken with a view to exploring the potentialities of ethyl formate as a non-aqueous solvent. Studies have also been extended to ethyl chloroformate, in order to examine the effect of replacement of hydrogen atom of formyl group in ethyl formate by chlorine atom, on its chemistry in general, and its solvent behaviour in particular.

Ethyl formate and ethyl chloroformate are colourless and transparent liquids which can be easily purified and are
not ordinarily affected by moisture or carbon dioxide. Some of their physical constants are given in Table I.

Table I: Physical constants of ethyl formate and ethyl chloroformate

<table>
<thead>
<tr>
<th>Property</th>
<th>Ethyl formate</th>
<th>Ethyl chloroformate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol. wt.</td>
<td>74</td>
<td>108.53</td>
</tr>
<tr>
<td>Melting point, °C</td>
<td>-78.9 (34)</td>
<td>-80.6 (34)</td>
</tr>
<tr>
<td>Boiling point, °C/760 mm</td>
<td>54.5 (35)</td>
<td>95.0 (34)</td>
</tr>
<tr>
<td>Density, g.ml⁻¹</td>
<td>0.94802 (36)</td>
<td>1.138 (34)</td>
</tr>
<tr>
<td>Viscosity, Poise at 20°</td>
<td>0.402 (34)</td>
<td>-</td>
</tr>
<tr>
<td>Surface tension, Dynes cm⁻¹ at 15°</td>
<td>-</td>
<td>27.5 ± 1 (37)</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>1.36975 (34)</td>
<td>1.392</td>
</tr>
<tr>
<td>Dipole moment, Debyes</td>
<td>1.93 ± 0.03 (34)</td>
<td>2.5</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>9.1 (38)</td>
<td>11.3 ± 0.03 (39)</td>
</tr>
<tr>
<td>Specific conductance, ohm⁻¹cm⁻¹ at 25°</td>
<td>3 x 10⁻⁷ (40)</td>
<td>1.2 x 10⁻⁸</td>
</tr>
<tr>
<td>Magnetic susceptibility (C.G.S. units)</td>
<td>-0.531 (34)</td>
<td>-</td>
</tr>
</tbody>
</table>

The convenient liquid range of ethyl formate and ethyl chloroformate is suggestive of the ease with which they may be handled. The value of dipole moment suggests that the compounds are polar in nature while their specific conductance indicates their feebly ionic character. Their
low dielectric constants are likely to have adverse effect on the solubility of ionic compounds in them. But compared to that of acetic acid (6.16 at 20°C) and ethyl acetate (6.40 at 22°C) their values are definitely higher and thus they are expected to be better solvents. In view of these properties, the two esters may serve as useful polar solvents.

The formation of complexes between carboxylic esters and inorganic halides is known since Damray's preparation of 1:1 adduct of titanium(IV) chloride with ethyl acetate (41) (in 1873) and a few adducts of ethyl formate with boron(III) fluoride (42) and chloride (43), antimony(V) chloride (44), zirconium(IV) chloride (45,46), bromide and iodide (47) have been reported.

Viscosity measurements of the mixtures of tin(IV) chloride (48) and bromide (49) with ethyl formate have revealed the existence of the adducts SnCl₄·2HCOOCH₂H₅ and SnBr₄·2HCOOCH₂H₅. Conductance measurements of the systems, silicon(IV) chloride-ethyl formate (50) and tin(IV) chloride - ethyl formate (50) at various temperatures have indicated the formation of complexes.

Dielectric constants of the mixtures of ethyl formate with germanium(IV) chloride and silicon(IV) chloride have been determined in benzene (51). Dielectric measurements of the addition compounds of zirconium(IV) chloride (46), bromide (52) and iodide (53) with ethyl formate have indicated that the addition compounds are highly polar in nature.
Dissociation constants of the Lewis acid adducts with ethyl formate have been determined cryoscopically in benzene (47, 52, 53).

Raman spectral studies of the mixture of tin(IV)chloride with ethyl formate have also been carried out (55). From the shift in the frequency of $C=O$ group, the donor function of the carbonyl group has been indicated and the compound has been assigned the following structure:

$$\text{H - C = O} \rightarrow \text{Sn} \rightarrow \text{O} \rightarrow \text{R} \rightarrow \text{Cl}$$

Infrared spectra of the addition compounds of antimony(III) chloride (56) and tin(IV)chloride (57) with ethyl formate, reveal that the carbonyl oxygen acts as a donor towards the Lewis acids. Mass spectra of deuterated ethyl formate have been compared with that of ethyl formate (58). From the appearance potential of $[\text{HCO(OH)}_2]$ ion, in the mass spectra of ethyl formate and isopropyl formate, the proton affinity of formic acid has been calculated.

Ethyl chlorofomate finds extensive applications for synthetic purposes. On being refluxed with bromine, it changes into ethylene dibromide (59). On treatment with silver nitrate, under mild conditions the nitrate ester has been obtained (60). The aliphatic and aromatic primary and secondary amines react
with ethyl chloroformate to yield urethans, in the presence of inorganic bases, which remove hydrogen chloride formed during the course of reaction (61). On treatment with \( \text{S}_{2} \) mercapto ethyl amines, ethyl chloroformate gives rise to dissubstituted products (61). Very recently it has been found that ethyl chloroformate on treatment with catalytic amounts of triphenyl phosphine, forms ethyl chloride, while with equivalent amounts of triphenyl phosphine the phosphonium chloride \((\text{C}_{6}\text{H}_{5})_{2}\text{P} \text{Cl}) \) is obtained (67). In aqueous solutions ethyl chloroformate undergoes hydrolysis producing ethyl alcohol and hydrochloric acid gas, although at 100°C, some ethylene is also formed (63). The hydrolysis is thought to proceed by a bimolecular displacement, to give rise to monoaalkyl carbonate, which rapidly decomposes in acid or neutral solution to produce alcohol as shown below:

\[
\text{EtOCCl} + \text{H}_2\text{O} \rightarrow \text{EtO}_2\text{COH} + \text{HCl}
\]

\[
\text{H}^+\text{EtO}_2\text{CO}^- \rightarrow \text{EtOH} + \text{CO}_2
\]

The following mechanism has been proposed for the second stage of the reaction:

The tertiary amines react vigorously with ethyl chloroformate to form quaternary ammonium compounds of the general
structure $\left[ \text{ROC}^0 \leftrightarrow \text{NR}_1 \text{R}_2 \text{R}_3 \right]^+ \text{Cl}^- \ (61,64)$.

The strong Lewis acids bring about decarboxylation of ethyl chloroformate and seem to act as catalysts as they do not undergo any change during the course of the reactions (65-67).

The infrared spectral studies carried out with a number of esters (57) have revealed that ethyl chloroformate is a very much weaker donor than the ethyl esters of unsubstituted acids.

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