INTRODUCTION

Non-aqueous solvent chemistry has made rapid advances in the last two or three decades. Reactions of the compounds, susceptible to hydrolytic attack in aqueous solutions, have been studied extensively in non-aqueous media, as a result of which a large number of chemical reactions, even for routine chemical preparations, are now being carried out in these solvents. Amongst the compounds which have been studied, mention must be made of liquid ammonia (1,2), liquid sulphur dioxide (3,4), methyl alcohol (5,6), glycolic mixtures (7,8), sulphuric acid (9,10), acetic acid (11-13), anhydrous hydrofluoric acid (14,15) and acetic anhydride (16,17). Even the acid chlorides like selenyl chloride (18,19), phosphoryl chloride (20,21), nitrosyl chloride (22,23), acetyl chloride (24,25) and benzoyl chloride (26,27) have been studied extensively for carrying out acid-base reactions. Acetic acid is next in importance to water as a medium for the estimation of organic bases (28), amides (29), alkaloids (30, 31) and other basic compounds, as these are insoluble in water and can be conveniently estimated in acetic acid medium. Primary, secondary and tertiary amines have been estimated even in their mixtures (32). Impressed by the successful study of the aforementioned solvents, an endeavour has been made in the present investigations, to explore the potentia-
Ethylacetate is a transparent, colourless and sweet smelling liquid. It can be easily purified and is not easily effected by the atmospheric moisture, carbon dioxide, etc. Some of its physical constants are given in Table I.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td>Melting point</td>
<td>-83.6°</td>
<td>(33)</td>
</tr>
<tr>
<td>Boiling point</td>
<td>77.15°</td>
<td>(33)</td>
</tr>
<tr>
<td>Density</td>
<td>0.92454 at 0°</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.89464 at 19°</td>
<td>(34)</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.37023 at 18.9°</td>
<td>(33)</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>6.4 ± 0.1 at 22°</td>
<td>(34)</td>
</tr>
<tr>
<td>Viscosity</td>
<td>108.8 c.p. at 28°</td>
<td>(35)</td>
</tr>
<tr>
<td>Specific conductivity</td>
<td>$1 \times 10^{-8}$ ohm$^{-1}$cm$^{-1}$</td>
<td>(36)</td>
</tr>
<tr>
<td>Dipole moment</td>
<td>1.84 at 25°</td>
<td>(37)</td>
</tr>
</tbody>
</table>

Availability in the pure state, the ease of handling and convenient working range are criteria for a good solvent. Thus ethylacetate may be a good solvent on the basis of these properties but its dielectric constant is quite low and this may have an adverse effect on the solubility of ionic compounds in it.

Naumann (38) was the first to study the solubilities of various compounds in organic solvents qualitatively. He also studied certain metathetical reactions in ethylacetate. By
passing dry hydrogen sulphide through the solutions of the chlorides of mercury and cadmium, he got sulphides and substituted sulphides of these metals.

$$3\text{HgCl}_2 + 2\text{H}_2\text{S} \rightarrow \text{HgS} + 4\text{HCl}$$

He also obtained insoluble ammonium chloride by passing hydrochloric acid gas in solution of ammonia in ethylacetate but he did not mention the role played by ethylacetate during the course of these reactions. With the recent development of the solvent theories, a new approach has been made towards the study of different chemical reactions in various solvents and the role played by these solvents is now being clearly understood.

The metal halides of the third and fourth groups of the Periodic Table are electron deficient and have a tendency to increase their coordination number by accepting electrons from some donor molecules. The existence of complexes between carboxylic esters and inorganic electron-deficient halides has been known since Demarcay's preparation of 1:1 adduct of titanium (IV)chloride and ethylacetate (39). A few complexes of the halides of the elements of groups III and IV with ethylacetate are reported in literature. Boron(III)fluoride (40,41) and chloride (42), tin(IV)chloride (43,44) and bromide (45), zirconium (IV)chloride (46,47), bromide (48) and iodide (49) form adducts with ethylacetate. It is observed that in the case of boron halides, the adducts formed with ethylacetate are 1:1 compounds whereas in the case of tin, titanium and zirconium, 1:2 complexes are preferentially formed.
Many physico-chemical investigations of the solutions of Lewis acids in ethylacetate have been carried out. Sugden and co-workers (50) studied the surface tension and parachor of the addition complex of boron(III)fluoride and ethylacetate. Kurnakov and Shternina (45) and Osipov and Suchkov (51) determined the conductivities of the solutions of tin(IV) chloride and ethylacetate and confirmed the existence of the complexes. Viscosity determination of the complex of tin(IV) chloride and ethylacetate was carried out by Osipov et al (51) and that of the solution of boron(III)fluoride and ethylacetate by Greenwood and Martin (52). Many other physical properties like dipole moment (53, 54), dielectric permeability (55), specific heat (45), heat of mixing (56), viscosity and fusibility (69) and transport of ions during electrolysis (57) have also been studied to explore the nature of these solutions.

Ethylacetate has two oxygen atoms which have lone pairs of electrons and thus can act as donors. The donor property of the two oxygen atoms in ethylacetate has been of great interest to various workers and attempts have been made to decide whether the acyl oxygen or the ethereal oxygen acts as the donor towards the electron-deficient halides. Halperin et al (58) studied the addition complexes of tin(IV) chloride with esters, ketones, aldehydes and ethers and observed that tin(IV)chloride derivatives of esters had the same stoichiometric composition as the adducts of ketones and aldehydes where acyl oxygen is the donor atom and they are
unlike the adducts of ethers where the ethereal oxygen is the donor atom.

Brown et al (59) studied the nature of the complexes of boron(III)fluoride with ethers, aldehydes, ketones and esters and observed that the stability of the adduct with ethylacetate was comparable to that of the ether adduct where ethereal oxygen is the donor and the adducts of aldehydes and ketones, where the donor character of acyl oxygen is not questioned, were not so stable. It was thus concluded that in these adducts of ethylacetate ethereal oxygen is the donor atom. In certain steroid hydroxy esters also the donor character of ethereal oxygen has been established (60). Baltzly et al (61), while explaining Fries rearrangement, supported the donor character of ethereal oxygen. From the products obtained as a result of the reaction between diborane and ethylacetate it is concluded that the first addition takes place at the ethereal oxygen (59). Ingold (62) has also proved that in the acid catalysed hydrolysis of the esters, the addition of the proton takes place at the ethereal oxygen and the same phenomenon is observed in the transesterification of esters. The donor property of ethereal oxygen in metal chelates has long been recognised in the derivatives of ethyl acetooacetate and methyl salicylate (63).

Greenwood and Martin (64) carried out the electrolysis of 1:1 compound of boron(III)fluoride and ethylacetate.
The ions responsible for the high conductivity of the solution have been represented as:

\[ \text{CH}_3\text{COOC}_2\text{H}_5\cdot\text{BF}_3 \rightarrow \text{H}^+ + (\text{CH}_3\text{COOC}_2\text{H}_4\cdot\text{BF}_3)^- \ldots \ldots (i) \]

or

\[ \text{CH}_3\text{COOC}_2\text{H}_5\cdot\text{BF}_3 \rightarrow \text{CH}_3\text{CO}^+ + (\text{OC}_2\text{H}_5\text{BF}_3)^- \ldots \ldots (ii) \]

The possibility of the existence of another mode of ionisation of the compound as represented by

\[ \text{CH}_3\text{COOC}_2\text{H}_5\cdot\text{BF}_3 \rightarrow \text{C}_2\text{H}_5^+ + (\text{CH}_3\text{COO}\cdot\text{BF}_3)^- \ldots \ldots (iii) \]

was ruled out on the basis of the results of electrolysis of the adduct between boron (III) fluoride and ethylacetate by Booth and Martin (65). Kuzmina et al (66) studied the conductivity of the solution of tin (IV) chloride in ethylacetate and on the basis of the electrolysis carried out by them, they attributed the high conductivity of the solution to the following possible ion pairs:

\[ \text{SnCl}_4\cdot2\text{CH}_3\text{COOC}_2\text{H}_5 \rightarrow (\text{SnCl}_2\cdot2\text{CH}_3\text{COOC}_2\text{H}_5)\text{Cl}_2 \rightarrow (\text{SnCl}_2\cdot2\text{CH}_3\text{COOC}_2\text{H}_5)^{2+} + 2\text{Cl}^- \]

Cryer (67) carried out Friedel-Crafts reaction between various esters and benzene using anhydrous aluminium (III) chloride as the condensing agent. Acetophenone was the product in the case of ethylacetate, though the yield was poor. The mechanism of the addition has been explained through the
formation of acetophenone established the existence of acetophenone (CH₃CO)⁺ ions, which further confirms the donor property of ethereal oxygen. Yashinolru and Haruo Shingu (68) carried out the condensation of esters with benzene in the presence of aluminium(III) bromide and found that for 1 mole each of benzene and aluminium(III) bromide, 0.41 mole of ester would react to form the ketone.

Quite recently Zackrisson and Lindqvist (70) have carried out the infra-red spectra studies of the addition complexes of ethylacetate with antimony(V) chloride, tin(IV) chloride and antimony(III) chloride and addition complexes of ethylformate with tin(IV) chloride and antimony(III) chloride. The shifts in ν(C=O) and ν(C-O) have been studied, and it has been shown that in these esters the carbonyl oxygen atom is the donor atom. Similar results have also been reported by Lappert (71) who examined the infra-red spectra of the addition complexes of metal halides and ethylacetate. It was found that carbonyl stretching vibrations are lowered in frequency but increased in intensity.
It is observed that usually $\nu(C = O)$ and $\nu(C - O)$ stretching frequencies are increased relative to those of pure ethylacetate but sometime $\nu(C - H)$ frequencies are also changed. He has also discussed the relative donor strength of various esters.

It is thus of great interest to investigate the nature of the complexes formed between the Lewis acids and ethylacetate and thus to establish the relative donor properties of the two oxygen atoms.

Apart from the tendency of Lewis acids to form adducts with compounds containing basic oxygen, protonic acids also have a tendency to form adducts with oxy-compounds like alcohols, aldehydes, esters, etc. Kastle (72) was the first to suggest, in 1896, the possibility of the formation of addition compounds between protonic acids and ethylacetate. This was later on confirmed by Bredig (73) and Rasenoff (74) who established the existence of an addition compound while explaining the mechanism of acid-catalysed hydrolysis of esters.

Maass and McIntosh (75) carried out the phase rule study of the two-component systems of organic oxygen compounds and halogens or halogen acids at low temperatures and detected the presence of many addition compounds between them.

Kendall and Gross (76) determined the conductivity of the solution of acetic and trichloroacetic acids in ethylacetate at various concentrations and confirmed the existence of addition compounds between the two components. Similar
results have been obtained by Kendall and Booge (77) in the phase rule study of these systems at low temperatures. Kendall and Brakeley (78) studied the change in the viscosity of the two component systems and confirmed the existence of the addition compounds as reported earlier.

The differentiating effect of anhydrous acetic and sulphuric acids on the strength of the protonic acids is well known (79,80). Hall (81) carried out potentiometric titrations between organic bases and various protonic acids in different solvents and compared the strength of perchloric, p-toluene sulphonic, and perfluorobutyric acids in ethylacetate by noting the heights of potential jumps at the neutralisation point.

Ionising solvents show certain common characteristic reactions, such as solubility of substances, formation of solvates, solvolytic reactions, existence of acids and bases and conductivity of such substances, conductometric titrations, potentiometric titrations and acid-base titrations in the presence of indicators. In the present investigations an effort has been made to study all such reactions in ethylacetate with a view to gathering information in support of the polar character of the pure solvent. An effort has also been made to study the nature of the addition complexes formed between the Lewis acids and ethylacetate and to elucidate their structures.

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