INTRODUCTION
Until recently water has been the favourite medium for the study of ionic reactions. It has some unique properties that make it an ideal solvent for ionic compounds. Consequently, chemistry of solvents other than water has taken that long to develop. Certain compounds are readily attacked by water and are difficult to be studied in aqueous medium. As a result, the seed of non-aqueous solvent chemistry was sown and during the last two or three decades it has flourished so much that it is now being regarded as a prominent and a specialised branch of chemistry.

Among the large variety of solvents which have been successfully recognised as non-aqueous media, mention may be made of liquid ammonia (1,2), liquid sulphur dioxide (3,4), acetic anhydride (5,6), acetic acid (7-9), methyl alcohol (10) etc. In these media, emphasis has been laid on the role played by the autoionisation of solvents while explaining the acid-base properties of various solutes in them. Acid-base reactions have also been carried out in ethylacetate (11) and methylformate (12) etc. A systematic study of electrolytic solvents using mixed organic solvents has been carried out by Fuoss (13). Acetic anhydride in mixture with nitromethane (14), acetonitrile (15), acetic acid and chloroform has been profitably used for the estimation of weak bases (16).

Organic acid halides take the distinction of being an
important group of compounds investigated as non-aqueous solvents. These include acid chlorides such as selenoyl (17), phosphoryl (18,19), nitrosyl (20), nitryl (21), sulphuryl (22), thionyl (23), acetyl (24) and benzoyl (25) chlorides. According to Allen and Sutton (26) the carbon-halogen bond in acetyl halides with the exception of fluorides, tends to be weaker as compared to those of the corresponding methyl halides. In mid sixtees, Meek and Drago(27) gave a different trend in explaining the solution chemistry in non-aqueous media and compelled workers in the field to reconsider their earlier observations.

Anhydrides such as acetic anhydride, sulphur dioxide and dinitrogen tetroxide have also been studied as non-aqueous media. The solvo system acetic anhydride has been extensively studied by Jander and his coworkers (28,29) followed by Paul and his coworkers (30) and Malhotra and his coworkers (31) laying emphasis on the importance of the equilibrium

$$\text{(CH}_3\text{CO)}_2\text{O} \rightleftharpoons \text{CH}_3\text{CO}^+ + \text{CH}_3\text{COO}^-$$

Jander and his coworkers (32) have postulated the existence of the ions such as

$$2\text{SO}_2 \rightleftharpoons \text{SO}^{2+} + \text{SO}_3^{2-}$$

in liquid sulphur dioxide. However, radio exchange studies do
not support the suggested autoionisation (33). A large number of oxy derivatives have been synthesised by the solvolysis of various metal and non-metal chlorides in it. Solution characteristics of liquid dinitrogen tetraoxide have established it as a good non-aqueous medium (34,35).

Strong protonic acids such as sulphuric acid (36-38), selenic acid (39), methanesulphonic acid (40), hydrofluoric acid (41,42), hydrochloric acid (43), chlorosulphuric acid (44) and fluorosulphuric acid (45-47) constitute another class of compounds which have been investigated as non-aqueous solvents. An important feature of solution chemistry in these highly acidic media is due to their weak nucleophilic character. Highly electrophilic species are stable in these weakly nucleophilic media. For example, many organic species which were postulated as reaction intermediates have been established and characterised in them. Unusual oxidation states of halogen cations have been established in these media (48,49). When selenium is heated at 60° in sulphuric acid, green solutions are formed due to the formation of $\text{Se}^2_8^+$ ions (50). The solutions turn yellow when oxidised with selenium dioxide due to the formation of $\text{Se}^4_4^+$ as

$$\text{Se}^2_8^+ + 5\text{H}_2\text{SO}_4 \rightarrow \text{Se}^4_4^+ + 2\text{H}_3\text{O}^+ + 4\text{HSO}_4^- + \text{SO}_2$$

Gillespie and his coworkers (51,52) have been successful in establishing the presence of cations of iodine, sulphur, selenium
and tellurium in fluorosulphuric acid. These cations have been prepared by the oxidation of these elements with peroxydisulphuryl difluoride in appropriate molar ratios. Selenium forms green solutions when oxidised with excess of peroxydisulphuryl difluoride, yellow solutions of $\text{Se}^{2+}$ are formed as

$$8\text{Se} + S_2O_6F_2 \rightarrow \text{Se}^2_8 + 2\text{SO}_3F$$

$$4\text{Se} + S_2O_6F_2 \rightarrow \text{Se}_4^{2+} + 2\text{SO}_3F$$

By removing excess of fluorosulphuric acid under reduced pressure, a yellow compound of composition $\text{Se}_4(\text{SO}_3\text{F})_2$ has been obtained (53). X-ray and spectral studies (54) have established it to be ionic compound with a square planar structure where the electrons are delocalised over the ring. A fascinating structure for the cation $\text{Se}_4^{2+}$ has been proposed as:

![Structure of Se$_4^{2+}$]

Hydrogen halides as non-aqueous solvents have limited liquid range (55-57). They are typical acceptor solvents. Due to the high acidity of the solvents, it is difficult to find the solvo acids of the systems. Covalent chlorides such as
boron trichloride behave as acid in hydrogen chloride and can neutralise tetraethylammonium dichloride as (58)

\[
\left[(\text{CH}_3)_4\text{N}\right]^+ \left[\text{HCl}_2\right]^– + \text{BCl}_3 \rightarrow \left[(\text{CH}_3)_4\text{N}\right]^+ \left[\text{BCl}_4\right]^- + \text{HCl}
\]

Waddington and his coworkers (59) carried out redox reactions in liquid hydrogen chloride and have been successful to oxidise phosphorus(III) and arsenic(III) compounds to 5+ oxidation state (60). Solvolytic reactions have also been reported in hydrogen chloride (loc cit).

Another distinct class of compounds investigated as non-aqueous solvents constitute carboxylic acids viz. formic acid (61), acetic acid (62) and its chloro derivatives (63, 64), propionic acid and heptafluorobutyric acid. Except formic acid the rest are nonpolar solvents. Formic acid has a high dielectric constant but has a poor donor number and is a suitable medium for studying complex ion reactions only if the ligand does not have the high proton affinity. Formic acid exerts a levelling effect on the basic properties of pyridine, benzidine, glycine, caffeine, urea, triphenyl carbinol, alcohol, ethers, acetanilide and propionitrile which behave as bases in it.

\[
\text{ROH} + \text{HCOOH} \rightarrow \text{R}^+ + \text{H}_2\text{O} + \text{HCOO}^–
\]

Fuoss and Shedlovsky (65) have determined \( \lambda_0 \) values of a number
of electrolytes and have determined the dissociation constants for weak electrolytes in it.

In the large list of non-aqueous solvents, one of the most extensively investigated solvents with a convenient working range and low viscosity is, acetic acid. Being a solvent with small dipole moment, low dielectric constant and strongly protogenic character, its solvent properties are not so appreciable as those of other solvents. A large number of organic and inorganic compounds readily form addition compounds with acetic acid (66). Pyridine forms compounds of varying composition with acetic acid (67, 68). Sulphur trioxide is known to form a compound of composition $\text{SO}_3 \cdot 3\text{CH}_3\text{COOH}$ with excess of acetic acid wherein sulphur is shown to have hexa-coordination (66), while Malhotra and his coworkers (69) have isolated a compound of composition $3\text{SO}_3 \cdot \text{CH}_3\text{COOH}$ which has been formulated as $\text{CH}_3\text{CO}^+ \cdot \text{HSO}_3^-$. Tin(IV) chloride forms a compound of composition $\text{SnCl}_4 \cdot 2\text{CH}_3\text{COOH}$ which has been formulated as a strong acid as $\text{H}_2 \left[\text{SnCl}_4(\text{OAc})_2\right]$. 

There are scattered references available in literature showing the formation of adducts of acetic acid with protonic acids (62, 70) which is quite unexpected of a solvent of low basicity. Paul and his coworkers (loc cit) have isolated an adduct of composition $\text{HSO}_3^\text{F} \cdot \text{CH}_3\text{COOH}$ with fluorosulphuric acid and this adduct has been developed as an acidic titrant for the estimation of weak bases. From a study of density, refractive
index, viscosity and specific conductance of binary system \( \text{H}_2\text{S}_2\text{O}_7\text{-CH}_3\text{COOH} \), Fialkov and Zhukarev (71) have established the existence of two compounds of composition \( \text{CH}_3\text{COOH}^+\text{HS}_2\text{O}_7^- \) and \( \text{CH}_3\text{COOH}^+\text{S}_2\text{O}_7^2- \).

Anhydrous acetic acid is a convenient solvent for carrying out acid-base neutralisation reactions conductometrically and potentiometrically (72). Lippincott and Timnich (73) have shown that acetic acid is a good solvent for high frequency titrations of substituted anilines and these titrations are comparable to the conductometric and potentiometric studies. Jander and Klaus (74) have carried out electrometric titrations in this medium. Redox reactions have been reported in acetic acid using cobalt(III) salts as strong oxidising agents (75).

Monochloroacetic acid exhibits all the characteristics of an ideal solvent with fairly high dipole moment and dielectric constant. Use has been made of its enhanced acidic strength to differentiate the acid strengths of various mineral acids (63). From conductance studies of the solution of monochloroacetic acid and ethylacetate (76), methylformamide (77) and ethylchloroformate (78) and dimethylformamide (79), Paul and his coworkers have shown the existence of their addition compounds. Chloroacetates of rare earth elements have been prepared and characterised wherein chloroacetates act as chelating bidentate group and there is polymerisation (80). Organotin carboxylates
have been prepared by various workers and their structures have been established (81). Malhotra and Sud have studied the nature of the solutions of protonic acids in it (82).

Methanol, because of its convenient liquid range, has long been used as a solvent in pure state or in mixture with other solvents. Bjerrum and his coworkers (83) have established its auto-ionisation as:

$$2\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OH}^+ + \text{OCH}_3^-$$

Paul and his coworkers (84) have studied the nature of the solutions of protonic acids and tertiary bases in methanol conductometrically and established that fluorosulphuric acid is an excellent titrant in this medium. Heats of solutions of various protonic acids have also been determined by Paul and his coworkers (85) and an order of relative acid and base strength has been proposed. Sulphuric acid has also been used as a titrant in methanol by Flowers and coworkers (86). Because of its donor character, it readily dissolves many acceptor halides. Conductance composition isotherms of the system boron trifluoride-methanol indicate the existence of 1:1 and 1:2 complexes of composition $\text{BF}_3\cdot\text{CH}_3\text{OH}$ and $\text{BF}_3\cdot2\text{CH}_3\text{OH}$ which have also been established by viscosity and density studies. In the molten state these compounds have been formulated as $\text{H}^+\left[\text{F}_3\text{B.OCH}_3\right]^{-}$ and $\left[\text{CH}_3\text{OH}_2\right]^+\left[\text{F}_3\text{B.OCH}_3\right]^{-}$ (87).
The reaction of a wide variety of Lewis acids such as boron(III) fluoride, trimethylborate, methyltrifluoracetate, nitromethane, ferric chloride etc. with the methoxide ion in methanol have been reported by Ludman and Waddington (88). Gutmann (89) has reported the results of potentiometric titrations of some chlorides against lithium methoxide in methanol. In the case of boron(III) chloride, species of the type $\text{B(OCH}_3)_3$ and $\text{B(OCH}_3)_4$ are formed. Niobium(V) and tantalum(V) chlorides yield the species $\text{M(OCH}_3)_5$, $\text{M(OCH}_3)_4^+$ and $\text{M(OCH}_3)_6^-$ etc. in methyl alcohol. Ethyl alcohol has also been used as a non-aqueous solvent. Most of the neutralisation reactions have been studied in a preparative way in ethyl alcohol. Solutions containing hydrogen chloride have been used for the formation of chloro complexes.

Phenol constitutes yet another class of bases which has not been fully explored as donor molecule. Metal phenoxides $\text{M(OPh)}_n$ where $\text{M}$ is a metal of valency $n$ may be considered as derived from phenol by the replacement of the phenolic hydrogen by the metal. Accordingly the chemistry of metal phenoxides like metal alkoxides, involves the study of M-O-C system. In contrast to alcohols, phenol has less tendency to form addition compounds with neutral ligands; the formation of phenolate complexes is greatly favoured due to its Brønsted acidity. Beryllium(II) chloride forms a phenoxide of composition $\text{Be(OC}_6\text{H}_5)_2$ with phenol (90). Diethyl beryllium on reacting
with highly hindered 2,6-di-t.butyl phenol results into a highly air sensitive monomeric compound where beryllium is only two coordinate (91). Cobalt(II) and nickel(II) phenoxides have also been isolated at -40°C from phenol and cyclopentadienyl salts of cobalt and nickel in toluene (92). Alkoxy and aryloxy derivatives of magnesium hydride of composition HMgOR are also known (93). Phenoxides of manganese(II) have also been reported by Prasad and coworkers (94). Some aryloxy coppers have been synthesised by the interaction of phenyl copper with phenols (95).

A number of workers have investigated the reaction of iron(III) chloride with phenol (96,97). Thermometric and conductance titration curves of iron(III) chloride and phenol show two breaks corresponding to Fe³⁺/phenol ratio of 1:3 and 1:6. But spectroscopic evidence shows the presence of a compound of composition Fe[Fe(0Ph)]₆. Moeller and coworkers (98) have suggested the possibility of the formation of a compound of composition Fe(0Ph)₃. Robinson and his coworkers (99) have shown that between pH 1.4-2.0 there is a reduction of Fe³⁺ to Fe²⁺ and it is accompanied by the formation of phenolic oxide. A series of bis(aryloxo) iron(II) and bis(alkoxo) iron(II) complexes of the type Fe(OC₆H₄X)₂.(bipy)₇Fe(OR)₂.(bipy)₇ with 2,2'-bipyridine ligand have been prepared by the reaction of diethyl bis(2,2'-bipyridine) iron(II) and corresponding substituted phenols or alcohols respectively. The phenoxo ligand is normally bonded to iron through oxygen (100).
Unlike the Υ bonding between ruthenium and phenoxy ligand in RnH(OC₆H₅)(PPh₃)₂ as observed by Wilkinson and his coworkers (101).

Some organophenoxy derivatives of aluminium such as dimethylphenoxyaluminium, methylphenoxychloroaluminium and phenoxydichloroaluminium have been reported recently (loc cit). They are all stable trimeric associated compounds but at higher temperatures, formation of a dimer is increasingly favoured. A compound of composition B(OPh)₃ is obtained when boron(III) chloride reacts with phenol at -70°C. Boron(III) phenoxide, unlike boron(III) alkoxide, has acceptor properties as it forms 1:1 addition compounds with organic tertiary bases (102).

Aryloxy derivatives of sulphur(VI) have been prepared by the reaction of arylsilyl ethers with sulphur(IV) fluoride and thionyl(IV) fluoride respectively (103,104). The products obtained depend upon the nature of the aryl group and also on the relative strength of the reactants.

Molybdenum oxyphenoxides of composition MoO(OPh)₄ are also known (105). Titanium(IV) chloride reacts with excess of pentafluorophenol at 25°C to yield a reddish brown compound of composition Ti(C₆F₅O)₄ but when titanium(IV) chloride is in excess, a red brown compound of composition Ti(OOC₆F₅)₂Cl₂ is obtained (106). Antimony(III) phenoxide (107), tungsten(VI) phenoxide (108) are also obtained by this method. Funk and his
coworkers (109) have prepared phenoxides of niobium(V), tantalum(V), molybdenum(V) and tungsten(VI) of composition Nb(0Ph)5, Ta(0Ph)5, W(0Ph)6, W(0Ph)4Cl2, Mo(0Ph)3Cl2 (110) by heating metal chlorides with an excess of phenol in a solvent. Tungsten(V) bromide when refluxed with appropriate amount of phenol in benzene yields W(0Ph)2Br3. Funk and Andrae (111) obtained monomeric compounds of composition U(OR)4·nNH3 where R is Ph, O-ClC6H4, O-NO2C6H4 and n = 1, 2 by a quantitative reaction of the corresponding phenol and ammonia with a suspension of uranium(IV) chloride in tetrahydrofuran. Phenoxides of composition U(0Ph)4 are obtained when tetrahydrofuran is replaced by benzene. Phenoxides of composition UO(0Ph)2·4PhOH·NH3 where Ph is either C6H5 or ClC6H4 are obtained when UOCl2 reacts with excess of phenol and ammonia in benzene.

A characteristic property of metal alkoxides is their ability to exchange an alkoxide group with alcohols as well as phenols. This property has been utilised extensively for the preparation of phenoxides of thallium (112), silicon (113), germanium (114), titanium (115), samarium (116), praseodymium and neodymium (117) and gadolinium and erbium (118).

\[
M(OR)_x + nPhOH \rightleftharpoons M(OR)_{x-n}(0Ph)_n + nROH
\]

Alcohols so liberated have a lower boiling point than phenol and can be removed by fractional distillation. The reaction can also be carried out in benzene which helps to remove the
alcohol so formed by azeotropic distillation. Mehrotra and his coworkers (115,118) have used this method profitably for the preparation of alkoxyphenoxy and phenoxy derivatives of the lanthanides. In an attempt to prepare U(OPh)₅ by the alcohol-phenol interchange method, Bagnall and his coworkers (119) obtained U(OPh)₄(OEt) when excess of phenol was refluxed with U(OEt)₅ for 9 hours. When refluxed for shorter period, a mixture of U(OPh)₃(OEt)₂ and U(OPh)₃(OEt) was obtained.

Metal phenoxides, like metal alkoxides, have poor acceptor properties which is in contrast to the pronounced acceptor properties of metal halides. This stems from the polymeric nature of many metal phenoxides in which the metal atom achieves coordination saturation via phenoxy bridging. Nevertheless, under suitable conditions, the intermolecular bridge can be ruptured and addition of another ligand can take place. Acceptor properties of the phenoxides of titanium are well established (120). Phenoxides of niobium(V) and tantalum(V) readily form addition compounds with oxygen and nitrogen bases (121). The Lewis acid character of metal phenoxides tends to be enhanced if some of the phenoxy groups are replaced by more electronegative substituents (122). The inductive effect of the phenyl ring favours adduct formation. Thus MeZn(OR) can be recovered unchanged from pyridine whereas MeZn(OPh) forms 1:1 adduct (123).

It is evident from the survey of literature that as compared
to acetic acid and methyl alcohol (Table I), no serious attempt seems to have been made to explore the potentiality of phenol as a non-aqueous solvent though scattered references are available about the use of alcohols as solvents. In the present studies, an endeavour has been made to explore the potentialities of fused phenol as a non-aqueous solvent and to compare its merit as a solvent with acetic acid.

Present studies have been divided into three chapters. First chapter deals with the solubility determination of a number of solutes, both ionic and covalent and Lewis acids and bases in phenol at $50 \pm 0.1^\circ C$. In some cases solvates of various solutes with phenol have been isolated and an effort has been made to characterise them. Behaviour of various protonic acids has been investigated in phenol and their relative strength has been compared in it. Equivalent conductance of a number of solutes at very low concentrations has been determined and $\lambda_0$ values have been calculated. Possibility of ion pair and triple ion formation has also been explored in fused phenol. Fluorosulphuric acid has been developed as an acidic titrant and a number of bases have been estimated in phenol.

Second chapter includes the behaviour of a number of metal chlorides in fused phenol. In order to explore the possibility of their phenoxide formation, conductometric titrations between metal chlorides and alkali
TABLE-I: Physical properties of methyl alcohol, ethyl alcohol, phenol and acetic acid

<table>
<thead>
<tr>
<th>Property</th>
<th>CH₃OH</th>
<th>C₂H₅OH</th>
<th>C₆H₅OH</th>
<th>CH₃COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point (°C)</td>
<td>-97.68</td>
<td>-114.5</td>
<td>45.5</td>
<td>16.83</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>64.75</td>
<td>78.33</td>
<td>186</td>
<td>118.1</td>
</tr>
<tr>
<td>Molecular volume 20°C</td>
<td>40.72</td>
<td>58.66</td>
<td>-</td>
<td>57.21</td>
</tr>
<tr>
<td>Density at 20°C gms/ml</td>
<td>0.792</td>
<td>0.789</td>
<td>1.092C</td>
<td>1.049</td>
</tr>
<tr>
<td>Dipole moment (Debye)</td>
<td>1.66</td>
<td>1.70</td>
<td>1.70</td>
<td>1.04</td>
</tr>
<tr>
<td>Dielectric constant at 20°C</td>
<td>31.2</td>
<td>25.0</td>
<td>9.7</td>
<td>6.1</td>
</tr>
<tr>
<td>Cryoscopic constant Kf</td>
<td>-</td>
<td>-</td>
<td>7.2</td>
<td>3.59</td>
</tr>
<tr>
<td>Specific conductance ohm⁻¹cm⁻¹</td>
<td>2.10 x 10⁻⁹</td>
<td>1 x 10⁻⁹</td>
<td>1.8 x 10⁻¹⁰</td>
<td>4 x 10⁻⁹</td>
</tr>
<tr>
<td>Autoprotolysis constant</td>
<td>-</td>
<td>10⁻¹⁹</td>
<td>-</td>
<td>10⁻¹³</td>
</tr>
<tr>
<td>Heat of fusion</td>
<td>5.7</td>
<td>6.6</td>
<td>11.4</td>
<td>2.8</td>
</tr>
</tbody>
</table>
metal phenoxides have been carried out in fused phenol to establish the formation of phenoxides. Acid-base neutralisation reactions between metal chlorides and organic tertiary bases have been carried out in fused phenol to explore the possibility of the role played by the autoionisation of the solvent. Reactions of acetyl chloride with metal phenoxides to get back the original metal chlorides has also been explored.

Third chapter deals with the preparation and characterisation of the phenoxides of selenium(IV), tellurium(IV), iodine(III) and antimony(V). Acceptor properties of these phenoxides have been established by reacting with alkali metal phenoxides and also by isolating their adducts with tertiary bases. Conductometric titrations between the solvo bases such as alkali metal phenoxides and the solvo acids such as selenium(IV), tellurium(IV) and antimony(V) phenoxides have also been carried out. Solvo base character of phenoxides of selenium(IV) and tellurium(IV) has been established by titrations with phenoxides of titanium(IV), tin(IV), aluminium(III) and niobium(V) and tantalum(V). A number of addition compounds between two types of phenoxides has also been isolated and characterised. Solvo base character of iodine(III) phenoxide has also been explored in fused phenol by reacting with a number of acids of the system.
REFERENCES