INTRODUCTION
Until recently water has been the favourite medium for the study of ionic reactions. There are certain unique properties of water that make it an ideal solvent for ionic compounds and it is largely due to these that the chemistry of solvents other than water has taken so long to develop. It has been only since the late twenties that the solution chemistry in non-aqueous solvents has been recognised as a separate and specialised branch of chemistry. Reactions of compounds susceptible to hydrolytic attack and even some routine chemical syntheses are now being extensively carried out in the non-aqueous media.

Chemistry of a large variety of non-aqueous solvents has been successfully explored and among these, mention may be made of such solvents as liquid ammonia (1-3), liquid sulphur dioxide (4-6), acetic anhydride (7-9), acetic acid (10-14), methyl alcohol (15, 16), etc. Acid-base reactions have been carried out in selenyl (17), nitrosyl (18), nitryl (19), sulphuryl (20), thionyl (21) phosphoryl (22), acetyl (23) and benzoyl chlorides (24). The use of these compounds as potential non-aqueous media has also been
of a great interest because of their successful use as reaction media for the preparation of anhydrous metal chlorides (25, 26).

Strong protonic acids such as sulphuric acid (27, 28), selenic acid (29, 30), disulphuric acid (31-33), hydrofluoric acid (34-37), hydrochloric acid (38-40) and difluorophosphoric acid (41) constitute another interesting class of compounds, which have been investigated as non-aqueous reaction media. Of all these, sulphuric acid has been studied most extensively. These strong acids are weakly nucleophilic in character and can stabilise strongly electrophilic cations which is one of the interesting features of the solution chemistry of these highly acidic media. For instance, the carbonium ions which were hypothetical intermediates in various organic reactions, have now been stabilised and characterised (42-44). High solvolysing power, high dielectric constant and their strong tendency to donate protons, help the dissolution of a large number of compounds in them.

The strong protonic acids generally have a high specific
conductance which is explained due to extensive self-ionisation of the solvents (Table 1). Most of the solutes dissolve forming highly conducting solutions. Transport measurements in these solvents indicate that the current is mainly carried by the cations and anions characteristic of the autoionisation of the solvents (45-47). The high conductance is explained in terms of the chain conduction mechanism. This finds support from the high viscosity of these media where the process of diffusion is bound to be extremely slow. Extensive and accurate work of Gillespie and coworkers (loc.cit) has enabled us to understand the fundamental properties of sulphuric acid solvent system.

Sulphuric acid has a tetrahedral structure where sulphur atom uses $sp^3$ hybrid orbitals. When one of the hydroxyl groups of the sulphuric acid molecule is replaced by fluorine, chlorine or a methyl group, it results in the formation of fluorosulphuric, chlorosulphuric or methanesulphuric acids respectively. Spectroscopic evidence (48-50) supports the tetrahedral structure of these acids. The strength of these acids is dependent
TABLE I

Physical properties of various strong protonic acids

<table>
<thead>
<tr>
<th>Properties</th>
<th>H$_2$SO$_4$</th>
<th>H$_2$S$_2$O$_7$</th>
<th>HSO$_3$F</th>
<th>HSO$_3$Cl</th>
<th>HSO$_3$CH$_3$</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freezing pt. °C</td>
<td>10.371</td>
<td>35.15</td>
<td>-88.98</td>
<td>-90.00</td>
<td>19.60</td>
<td>-89.37</td>
</tr>
<tr>
<td>Boiling pt. °C</td>
<td>290-317</td>
<td>--</td>
<td>162.70</td>
<td>152.10</td>
<td>165.00/5 mm</td>
<td>19.51</td>
</tr>
<tr>
<td>Density g/ml</td>
<td>1.82</td>
<td>1.96</td>
<td>1.72</td>
<td>1.76</td>
<td>1.46</td>
<td>1.06</td>
</tr>
<tr>
<td>Viscosity (centipoise)</td>
<td>25.54</td>
<td>74.86</td>
<td>1.56</td>
<td>--</td>
<td>10.52</td>
<td>0.95 at 0°C</td>
</tr>
<tr>
<td>Dielectric constant at 25°C</td>
<td>100.00</td>
<td>50.00</td>
<td>130.00</td>
<td>60.00</td>
<td>--</td>
<td>111.00 at -27°C</td>
</tr>
<tr>
<td>Sp. cond. (Ohm$^{-1}$cm$^{-1}$) at 25°C</td>
<td>1.04x10$^2$</td>
<td>3.70x10$^3$</td>
<td>1.08x10$^{-4}$</td>
<td>1.60x10$^{-3}$</td>
<td>0.40x10$^{-2}$</td>
<td>1.40x10$^{-6}$ at 0°C</td>
</tr>
<tr>
<td>Cryoscopic constant</td>
<td>6.12</td>
<td>5.90</td>
<td>3.93</td>
<td>--</td>
<td>--</td>
<td>1.40</td>
</tr>
<tr>
<td>$H_0$ value</td>
<td>-11.00</td>
<td>--</td>
<td>-12.08</td>
<td>--</td>
<td>-7.86</td>
<td>-10.20</td>
</tr>
</tbody>
</table>
upon the electronegativity of the substituted group, for example, fluoro- and chlorosulphuric acids are stronger whereas methanesulphuric acid is weaker than sulphuric acid (51, 52). In order to compare the relative merit of various acids as solvents, physical properties of all the strong protonic acids have been included in Table 1. The structures of the various substituted sulphuric acids and sulphuric acid are as given below:

\[
\begin{align*}
\text{Sulphuric acid} & : & \text{HO-SO}_3^+ \\
\text{Fluorosulphuric acid} & : & \text{HO-SF}_2^+ \\
\text{Chlorosulphuric acid} & : & \text{HO-SCl}_2^+ \\
\text{Methanesulphuric acid} & : & \text{H}_3C-SO_3^+
\end{align*}
\]

A comparative study of the physical constants of various strong protonic acids suggests that fluorosulphuric acid is a better solvent than methanesulphonic acid. Fluorosulphuric acid has a convenient working range and a very high dielectric constant. Its viscosity is much less than that of sulphuric acid and hence most of the solutes dissolve readily in this solvent. Its $H_0$ Hammet's acidity
function) value is -12.8, which is rather high. All these properties make it a strongly acidic solvent.

Fluorosulphuric acid was known to Thorpe as early as 1892 (53). Since 1928, a convenient method of its preparation in the laboratory (54) has inspired interest in its chemistry as a solvent. However, it was only recently that the use of fluorosulphuric acid as a solvent was made by Woolf (55, 56). Paul and coworkers (57, 58) have established on the basis of the conductance and thermo-chemical investigations in differentiating solvents like acetic acid, that fluorosulphuric acid is even stronger an acid than perchloric acid. It has been found to be a better substitute for perchloric acid in the estimation of nitrogenous bases in the non-aqueous media. Gillespie and coworkers (59, 60) have explored its potentialities as a reaction media to some extent.

Pure fluorosulphuric acid has a fair high conductance indicating that it is a highly self-ionise solvent. The possible modes of its ionisation may be represented as:

\[
2\text{HSO}_3\text{F} \rightleftharpoons \text{H}_2\text{SO}_3\text{F}^+ + \text{SO}_3\text{F}^- \quad \ldots \text{(a)}
\]

\[
2\text{HSO}_3\text{F} \rightleftharpoons \text{H}_2\text{F}^+ + \text{S}_2\text{O}_6\text{F}^- \quad \ldots \text{(b)}
\]
The possibility of the equilibrium (b) has been ruled out by Gillespie and coworkers (46) and it has been established that the conductance of the pure solvent is mainly due to the equilibrium (a) which has an autoprotolysis constant (Ka) of the order of $10^{-7}$ Mole$^{-2}$ Kg$^{-2}$. Cryoscopic investigations (61) have also ruled out the molecular self-dissociation of fluorosulphuric acid as:

$$HSO_3^F \rightleftharpoons HF + SO_3$$

According to the solvent system concept, those substances which increase the concentration of the fluorosulphuric acidium ions, ($H_2SO_3F$)$^+$, directly or indirectly, behave as acids and those which increase the concentration of the fluorosulphate ions, ($SO_3F$)$^-$, behave as bases in this solvent. Accordingly, the alkali and the alkaline earth metal fluorosulphates, therefore, behave as strong bases in fluorosulphuric acid. From the similarity in the conductance of the univalent and divalent fluorosulphates, it has been postulated that the current is mainly carried by the fluorosulphate ions. This finds support from the small values obtained for the transport
number of cations for the solutions of alkali and alkaline earth metal fluorosulphates.

Fluorosulphuric acid is a strongly hydrogen bonded molecule and the effective movement of the $H_2SO_3F^+$ and $SO_3F^-$ ions may be visualized as:

\[
\begin{align*}
\text{F} & \quad \text{OH} \\
\text{S} & \quad \text{0} \\
\text{O} & \quad \text{0} \\
\end{align*}
\begin{align*}
\text{F} & \quad \text{OH} \\
\text{S} & \quad \text{0} \\
\text{O} & \quad \text{0} \\
\end{align*}
\begin{align*}
\rightarrow & \\
\text{F} & \quad \text{O}^- \\
\text{S} & \quad \text{0} \\
\text{0} & \quad \text{0} \\
\end{align*}
\begin{align*}
\text{F} & \quad \text{OH} \\
\text{S} & \quad \text{0} \\
\text{O} & \quad \text{0} \\
\end{align*}
\begin{align*}
\text{F} & \quad \text{OH} \\
\text{S} & \quad \text{0} \\
\text{O} & \quad \text{0} \\
\end{align*}

That the current is carried by the $H_2SO_3F^+$ ions has been explained by the chain conduction mechanism (Fig. 1). Similar mechanism of conduction has earlier been proposed in case of water, sulphuric (62) and chlorosulphuric (63) acids. Due to high mobilities of the $H_2SO_3F^+$ and $SO_3F^-$ ions, the electrical conductivities of various solutes in fluorosulphuric acid are principally determined by the number of $H_2SO_3F^+$ and $SO_3F^-$ ions produced per mole of the solute. Thus measurements of electrical conductances provide valuable information concerning the mode of ionisation of various electrolytes.
FIG. 1 GROTHUS CHAIN MECHANISM.
The high acidity of fluorosulphuric acid and its low freezing point have been profitably used by Gillespie and coworkers (64, 65) in n.m.r. studies of the protonation of weak bases and their findings have characterized the site of the protonation of these bases. It has been shown in the case of amides that at very low temperatures, the site of protonation is the carbonyl oxygen and not the nitrogen atom (66). It has also been observed that a solution of phenol in fluorosulphuric acid is protonated at the para position of the aromatic ring and not on the oxygen atom (64). The possible structure of the protonated phenol has been represented as:

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{OH} \\
\text{H} & \quad \text{OH} \\
\text{H} & \quad \text{C} \quad \text{O} \\
\end{align*}
\]

Due to a high acidity of the solvent, it has been very difficult to find a substance which would behave as an acid in the fluorosulphuric acid solvent system. Woolf (56) carried out conductimetric titrations between antimony pentafluoride and potassium fluor sulphate and concluded that antimony pentafluoride behaves as a weak
acid in this system as represented below:

$$\text{SbF}_5 + \text{SO}_3\text{F}^- \rightarrow \text{F}_5\text{Sb(SO}_3\text{F})^-$$

The SbF$_5$(SO$_3$F)$^-$ ion has been shown to contain hexa co-ordinated antimony, e.g.,

However, n.m.r. spectrum of this anion (67) supports the existence of a dimer, where two square pyramid SbF$_5$ groups are linked through a fluorosulphate bridge as represented below:

Furthermore, it has been shown (67) that by the addition of sulphur trioxide to a solution of antimony pentafluoride in
fluorosulphuric acid, a stronger acid of composition $\text{H}[\text{SbF}_2(\text{SO}_3\text{F})_4]$ is obtained, which ionises in fluorosulphuric acid as:

$$\text{H}[\text{SbF}_2(\text{SO}_3\text{F})_4] + \text{HSO}_3\text{F} \rightleftharpoons \text{H}_2\text{SO}_3\text{F}^+ + \text{SbF}_2(\text{SO}_3\text{F})_4^-$$

This highly acidic mixture has been called the "super acid". The formation of other acids such as $\text{H}[\text{SbF}_4(\text{SO}_3\text{F})_2]$, $\text{H}[\text{SbF}_3(\text{SO}_3\text{F})_3]$ and $\text{H}[\text{SbF}_2(\text{SO}_3\text{F})_4]$ has also been confirmed by $^{19}\text{F}$ n.m.r. measurements. In their search for stronger acids of fluorosulphuric acid solvent system, Gillespie and coworkers (68) have investigated the behaviour of pentafluorides of phosphorus, arsenic, bismuth and niobium in fluorosulphuric acid. It has been found that all of them act as weak electrolytes in fluorosulphuric acid. Even their mixtures with sulphur trioxide do not seem to enhance the acidity. Only a mixture of arsenic pentafluoride and sulphur trioxide (AsF$_5$:SO$_3$, 1:3) seems to form a reasonably strong acid. From the conductimetric titrations, the relative order of strength of these acids has been determined as:

$$\text{PF}_5 < \text{NbF}_5 < \text{AsF}_5 < \text{AsF}_4(\text{SO}_3\text{F}) < \text{SbF}_5 < \text{AsF}_2(\text{SO}_3\text{F})_3 < \text{SbF}_2(\text{SO}_3\text{F})_3.$$
Olah and coworkers (69, 70) have extensively used the highly acidic medium of SbF$_5$/HSO$_3$F/SO$_2$ for the preparation and identification of various conjugate acids and carbonium ions. Many previously unobserved cations have now been found to be stable at low temperatures. Wienstein and coworkers (71) have shown that, at low temperature, in super acid, there are two isomers of protonated acetic acid species which undergo a slow first order cleavage to give the oxomethyl carbonium ion. Similarly, two forms of protonated aldehydes have also been reported (72). Diphenylethyl (73) and methylethylphenyl (74) carbonium ions have been stabilised from the corresponding alcohols in this media. Carbonium ions such as protonated mono-, di- and tri-fluoro benzonium ions, alkinyl carbonium ions (75) and fluorocarbonium (76) ions have also been stabilised in the "super acid" medium.

Recently, new type of diprotonated ca ions have been
obtained by Olah and coworkers (77) from lipophilic glycols and diketones, at low temperatures. However, at room temperature, a rearrangement takes place and only the mono protonated species are obtained. At low temperature, a new type of halonium ion has been characterised (78) viz:

\[
\text{CH}_3\text{C} = \text{CH}_2 + \text{SbF}_5 \xrightarrow{-78^\circ \text{C}} \text{CH}_3\text{C} = \text{CH}_2 + \text{SbF}_6^-
\]

In addition to its importance in the study of new organic cations, fluorosulphuric acid has proved to be a very useful solvent for the preparation and investigation of some unusual homoatomic inorganic cations. The unusual cations of iodine (79), selenium (80), sulphur (81) and tellurium (82) have already been stabilised in fluorosulphuric acid. Even halogens, which are strongly electronegative, form cations of the type Br$_2^+$ (83) and Cl$_2^+$ (84) in this medium.

Fluorosulphuric acid is an excellent fluorinating agent and reacts with many oxides, oxy acids and their salts (85). Oxyfluorides are the usual products of these reactions but sometimes a fully fluorinated product is so obtained.
Engelbrecht and coworkers (86) have suggested that phosphorus pentoxide reacts with fluorosulphuric acid to form phosphoryl fluoride:

\[ \text{P}_2\text{O}_5 + 3\text{HSO}_3\text{F} \rightarrow \text{PO}_3\text{F} + \text{HPO}_3 + 2\text{SO}_3 + \text{H}_2\text{SO}_4 \]

However, arsenic pentoxide (87) is converted to a mixture of arsenic pentafluoride, arsenic difluoridetrifluorosulphate and arsenic trifluoridet trifluorosulphate while arsenic trioxide (88) forms only arsenic trifluoride. Barium selenate (89) when heated with fluorosulphuric acid forms selenyl difluoride whereas barium tellurate (90) forms monohydroxy tellurium pentafluoride.

It is noteworthy that the fluorinating property of fluorosulphuric acid is predominant only at elevated temperatures. Potassium perchlorate behaves as a base in fluorosulphuric acid, at 25°C, but on heating to 50-80°C, perchloryl fluoride distils over in quantitative yields (85). In case of potassium permangenate (91) and dichromate (92), fluorinating reaction is very exothermic and takes place even at the room temperature.

Permanganyl fluoride, MnO$_3$F, is obtained according to
the reaction:

$$\text{KMnO}_4 + 2\text{HSO}_3\text{F} \rightarrow \text{MnO}_3\text{F} + \text{KSO}_3\text{F} + \text{H}_2\text{SO}_4$$

but it is not stable above the room temperature and decomposes to give MnF$_2$, MnO$_2$ and O$_2$.

Metal fluorosulphates have been easily prepared by the action of sulphur trioxide with metal fluorides (93) but because of the high solvolysing property of fluorosulphuric acid, it has also been utilised for the preparation of various metal fluorosulphates. Woolf (94) has successfully prepared the transition metal fluorosulphates by the interaction of metal acetates, sulphates and halides with fluorosulphuric acid. The ease of the displacement reaction has been found to follow the order $\text{CH}_3\text{COO}^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{F}^-$. It has been further suggested that the displacement reaction is the easiest when the change in the molecular volume is the least. Acetates are very close to the fluorosulphates in molecular volume whereas fluorides are the farthest apart.

As compared to fluorosulphuric acid, little work has been done in chlorosulphuric acid as a solvent, possibly
Moreover, chlorosulphuric acid is weaker than fluorosulphuric acid due to the lower electronegativity of chlorine compared to fluorine. Paul et al (51) and Robinson et al (96) have postulated its mode of self-ionisation to be analogous to that of fluorosulphuric acid:

\[ 2\text{HSO}_3\text{Cl} \rightleftharpoons \text{H}_2\text{SO}_3\text{Cl} + \text{SO}_3\text{Cl}^- \]

Boron trichloride (96) behaves as an acid of this system and metal chlorosulphates act as bases. Although it is weaker than fluorosulphuric acid, yet it is stronger than sulphuric acid, and has been utilise to stabilise certain carbonium ions (97). Waddington and coworkers (98) while carrying out acid-base reactions in anhydrous hydrochloric acid, have shown that chlorosulphuric acid behaves as an acid of the solvent and the ionisation may be represented as follows:

\[ \text{HSO}_3\text{Cl} + \text{HCl} \rightleftharpoons \text{H}_2\text{Cl}^+ + \text{SO}_3\text{Cl}^- \]

This has been supported by Robinson and coworkers (96) from conductance measurements in chlorosulphuric acid,
they have shown that hydrochloric acid behaves as a weak base of this solvent system.

In contrast to sulphuric acid, chlorosulphuric and fluorosulphuric acids, very little is known about the nature of methanesulphuric acid. Though methanesulphuric acid has been frequently used in synthetic organic chemistry in sterically sensitive sulphonation reactions (99), yet no attempt seems to have been made to explore its utility as a solvent. It has an adverse effect on the male reproductive system. Nevertheless methanesulphuric acid finds applications in biochemical and various pharmaceutical reactions.

An attempt as early as 1929 was made by Berthoud (100) to determine the physical constants of methanesulphuric acid, but since then no serious effort seems to have been made to study its chemistry in detail. High viscosity, high freezing point and surface tension (Table I) support the speculation that there is a strong intermolecular hydrogen bonding between the molecules of methanesulphuric acid. The acid is not very hygroscopic and can be
conveniently handled. It does not affect loss and when stored in air-tight flasks, can be kept for weeks without any change in the conductance of the solution.

Methanesulphuric acid has an $H_{\text{o}}$ value of -7.86 (101) which is higher than that of nitric acid, -6.3 (102), but is far lower than that of sulphuric and fluorosulphuric acids (cf. Table 1). This relative order of the acid strength has been supported by the dissociation constants of these acids in aqueous solutions (103). Gillespie and coworkers (104) from the conductance studies in sulphuric acid have suggested that methanesulphuric acid is as strong an acid as selenic acid. Caro and Cefola (105), considering its acidic strength, have used it as an acidic titrant in carrying out acid-base titrations in non-aqueous media and excellent results have been obtained in potentiometric and visual titrations.

The system $\text{SO}_3^-\text{CH}_3\text{SO}_3\text{H}$, has been investigated by Robinson and coworkers (106). The n.m.r. studies indicate that initially pyromethanesulphuric acid is formed, which with an excess of sulphur trioxide forms $(\text{CH}_3)_2\text{SO}_5$ and $\text{H}_2\text{SO}_4$. It has been found that in the presence of excess of sulphur
trioxide, three types of polymers of general composition $\text{CH}_3\text{Sn}^{+3n+3}\text{H}_n$, $(\text{CH}_3)_2\text{Sn}^{+203n+5}$ and $\text{H}_2\text{Sn}^{+103n+4}$ are present.

The first attempt to explore its potentialities as a reaction media was made by Newman and coworkers (107) who investigated cryoscopically the behaviour of strong bases in methanesulphuric acid and found that they were completely ionised. Since then not many investigations have been reported on methanesulphuric acid. Literature lacks information on any conductimetric investigations in this solvent. Since selenic acid, which is as strong an acid as methanesulphuric acid has been investigated as the reaction media (29) and some acid-base reactions have been reported to prove its autoionisation, therefore, it is worthwhile to explore the potentialities of methanesulphuric acid as a solvent, and also to prove its mode of autoionisation.

Lot of investigations have been reported to explore the potentialities of sulphuric acid as a solvent but as compared to it, very little work has been carried out in substituted sulphuric acids. Therefore, in the present
investigations, an endeavour has been made to explore the utilities of substituted sulphuric acid as the reaction media. The present investigations have been restricted to two solvents only. Fluorosulphuric acid and methanesulphuric acid mainly because of the excellent solvent properties of the former and the lack of available data in the case of the latter.