SUMMARY
As compared to acetic acid, dibromoacetic acid is a better proton donor molecule. Its dielectric constant and dipole moment values are higher than those of acetic acid but its solvent potentialities have not yet been explored. In the present studies, its use as a non-aqueous medium has been investigated. The first step in the study of a solvent involves the solubility determinations. Solubilities of a large number of compounds, both organic and inorganic, have been determined at 60±0.5° C in it. It is observed that as compared to ionic compounds, covalent compounds are more soluble in it. Iodides have been found to be more soluble than the bromides and chlorides of the same metal. Lewis acids and bases are either completely miscible or highly soluble in this medium. Tetraalkyl ammonium salts are highly soluble in it and when they are added in excess, corresponding dibromoacetates are obtained. Tetrachlorides of selenium and tellurium undergo reduction in it to form black powder.

Dibromoacetic acid forms solvates with a large number of compounds including lewis acids and organic tertiary bases. The solvate formation has been established by actual isolation of the solvates and also by conductometric measurements. The solutions of lewis acids and organic tertiary bases have been found to be highly conducting which shows the presence of ions in the solutions. From infra-red spectra and solution chemistry of these compounds in various aprotic and protonic solvents, possible structure of these adducts have been proposed. In the case of the adducts of lewis acids, carbonyl oxygen of dibromoacetic acid has been shown to be the donor site and the possible ions present in the solid state and in solutions are:

\[
\begin{align*}
    MX_4 + 2\text{CHBr}_2\text{COOH} &\rightarrow MX_4\cdot2\text{CHBr}_2\text{COOH} = 2H^+ (\text{solvated}) + [MX_4(\text{CHBr}_2\text{COO})_2]^2^- \\
    MX_3 + \text{CHBr}_2\text{COOH} &\rightarrow MX_3\cdot\text{CHBr}_2\text{COOH} = H^+ (\text{solvated}) + (MX_3 \text{ CHBr}_2 \text{ COO})^-
\end{align*}
\]

The compounds BBr_3 CHBr_2 COOH and SbCl_5 CHBr_2 COOH have been found to be fairly strong protonated acids. By determining the equivalent conductance values of these compounds in acetic acid at low concentrations, their relative acid strength with other minerals acids has been compared. The order of their decreasing acid strength is:

\[
    \text{HSO}_3\text{F} > \text{HClO}_4 > \text{HSO}_3\text{Cl} > \text{BBr}_3 \text{ CHBr}_2\text{COOH} > \text{SbCl}_5 \text{CHBr}_2\text{COOH} > \text{HBr} > \text{H}_2\text{SO}_4 > \text{HCl}
\]
In the case of the adducts of organic tertiary bases with fused dibromoacetic acid, conductance and infrared spectral studies show the presence of ions as:

\[ \text{B} + \text{CHBr}_2\text{COOH} \rightarrow \text{B.CHBr}_2\text{COOH} \quad \text{BH}^+ + \text{CHBr}_2\text{COO}^- \]

Acid base titrations between antimony pentachloride and pyridine have been carried out in fused dibromoacetic acid. These titrations have been followed conductometrically, potentiometrically and with the help of visual indicators to prove the role played by the autoionization of the solvent. A typical acid-base reaction in fused dibromoacetic acid can be explained as,

\[ \text{CHBr}_2\text{COOH}_2^+ + \text{SbCl}_5\text{CHBr}_2\text{COO}^- + \text{BH}^+ + \text{CHBr}_2\text{COO}^- \rightarrow \]
\[ \text{BH}^+ + \text{SbCl}_5\text{CHBr}_2\text{COO}^- + 2\text{CHBr}_2\text{COOH}. \]

Solvolytic reactions between fused dibromoacetic acid and oxides, carbonates, oxalates, formates, sulphites, nitrites, nitrates and chlorides of metals, form the corresponding dibromoacetates. Oxides of zinc, cadmium and mercury form the dibromoacetates of composition \( \text{M(CHBr}_2\text{COO)}_2 \\text{CHBr}_2\text{COOH} \). From infrared and conductance studies, it is observed that the carboxylate group acts as bridging as well as chelating group and the central metal atom acquires a coordination number of six. Oxides of nickel, cobalt and copper form the corresponding dibromoacetate of composition \( \text{M(CHBr}_2\text{COO)}_2 \) and the central atom is found to have a tetrahedral structure. Adducts of Pyridine N-Oxide and triphenylphosphineoxide with dibromoacetates of cobalt and nickel have been isolated and characterized. Trichlorides of Phosphorous, arsenic, antimony and bismuth form the compound \( \text{P}_3\text{(CHBr}_2\text{COO)}_2 \text{, As(CHBr}_2\text{COO)}_3 \text{, SbCl}_2\text{(CHBr}_2\text{COO) and BiCl}_2\text{(CHBr}_2\text{COO) when refluxed with excess dibromoacetic acid for 12 to 15 hrs. The compound P}_3\text{(CHBr}_2\text{COO)}_2 \text{could not be characterized while the compound As(CHBr}_2\text{COO)}_3 \text{has been found to be covalent one where arsenic does not seem to acquire a coordination number of four or six. The compounds SbCl}_2\text{(CHBr}_2\text{COO) and BiCl}_2\text{(CHBr}_2\text{COO) have tetra coordinated central metal atom. When the trichlorides are refluxed for longer period then compounds of composition Sb(CHBr}_2\text{COO)}_3\text{CHBr}_2\text{COOH and Bi(CHBr}_2\text{COO)}_3\text{CHBr}_2\text{COOH are obtained. The possible reactions for the formation of these}}

\[ \text{PrCHBr}_2\text{COOH}_2^+ + \text{SbCl}_5\text{CHBr}_2\text{COO}^- + \text{BH}^+ + \text{CHBr}_2\text{COO}^- \rightarrow \]
\[ \text{BH}^+ + \text{SbCl}_5\text{CHBr}_2\text{COO}^- + 2\text{CHBr}_2\text{COOH}. \]
Summary

dibromoacetates from the metal chlorides involving the ions of the solvent may be formulated as:

\[ \text{MCI}_3 + 2\text{CHBr}_2\text{COOH} \quad \text{reflux} \quad \text{MCI}_3\cdot\text{CHBr}_2\text{COO}' + \text{CHBr}_2\text{COOH}_2^+ \]

Further refluxing of the intermediates in excess of the solvent replace the other chlorine atoms bonded to the metal and the final product is a completely solvolysed compound \( \text{M(CHBr}_2\text{COO})_3 \). All these reactions, described above through the existence of \( \text{CHBr}_2\text{COO}' \) ions in solution supporting the auto ionisation of fused dibromoacetic acid as:

\[ 2\text{CHBr}_2\text{COOH} \quad \text{\rightarrow CHBr}_2\text{COOH}_2^+ + \text{CHBr}_2\text{COO}^- \]

Solvolytic reactions of tetrachlorides of tin, titanium, zirconium, thorium and silicon with excess of fused dibromoacetic acid have been carried out and compounds of composition \( \text{SnCl}_2(\text{CHBr}_2\text{COO})_2, \text{Ti(CHBr}_2\text{COO})_4, \text{Zr(CHBr}_2\text{COO})_4, \text{Th(CHBr}_2\text{COO})_2 \) and \( \text{Si}_2\text{O(CHBr}_2\text{COO})_6 \) have been isolated. From infrared, molecular weight and conductance studies, their structures have been elucidated. Their Lewis acid character has been established by isolating and characterization of their adducts with organic tertiary bases. Antimony pentachloride, aluminium trichloride and ferric chloride form compounds of composition \( \text{SbCl}_2(\text{CHBr}_2\text{COO})_3, \text{Al(CHBr}_2\text{COO})_3, \text{FeCl(CHBr}_2\text{COO})_2 \) and \( \text{Fe(CHBr}_2\text{COO})_3 \) when refluxed with excess of the solvent and these compounds have been characterized by conductance and infrared spectral studies. A possible course of reactions involving the liberation of HCl may be proposed as:

\[ \text{MCI}_4 + \text{CHBr}_2\text{COOH} \quad \Rightarrow \quad \text{MCI}_4\cdot\text{CHBr}_2\text{COOH} \]

\[ \text{MCI}_4\cdot\text{CHBr}_2\text{COOH} + \text{CHBr}_2\text{COOH} \quad \text{reflux} \quad \text{MCI}_4\cdot\text{CHBr}_2\text{COO}' + \text{CHBr}_2\text{COOH}_2^+ \]

Similarly other chlorine atoms may be replaced by dibromoacetate groups. In the case of silicon tetrachloride basic dibromoacetate \( \text{Si}_2\text{O(CHBr}_2\text{COO})_6 \) is formed. In the beginning the reaction is straight forward but the side reactions of the type shown below also take place:
Redox reactions have also been carried out in fused dibromo acetic acid and some reducing agents such as thiourea, phenylhydrazine, ascorbic acid when titrated against some oxidizing agents as potassium permanganate, potassium dichromate, bromine, iodine monochloride, potassium ferricyanide could easily be estimated in it. Some elements has also been oxidized to the higher oxidation states with the help of these oxidizing agents. Lead tetradibromoacetate has been used to oxidise tin (II), antimony (III), arsenic (III) and phosphorous (III) to higher oxidation states as:

\[ \text{Pb}^{4+} + \text{Sn}^{2+} \rightarrow \text{Pb}^{2+} + \text{Sn}^{4+} \]
\[ \text{Pb}^{4+} + \text{As}^{3+} \rightarrow \text{Pb}^{2+} + \text{As}^{5+} \]

It also oxidizes cobalt (II) and nickel (II) to (III) oxidation states as:

\[ \text{Pb}^{4+} + 2\text{Co}^{2+} \rightarrow \text{Pb}^{2+} + 2\text{Co}^{3+} \]
Similarly iodine has been successfully developed as oxidizing agent in this medium. Potassium permanganate and potassium dichromate act as fairly good oxidizing agent for the redox reactions in this solvent. These redox reactions have been followed potentiometrically. From the potential jumps the following reactions have been proposed as:

\[
\begin{align*}
2\text{Cr}^{6+} + 3\text{Sn}^{2+} & \rightarrow 2\text{Cr}^{3+} + 3 \text{Sn}^{4+} \\
\text{Cr}^{6+} + 3\text{Fe}^{2+} & \rightarrow \text{Cr}^{3+} + 3 \text{Fe}^{3+} \\
2\text{Mn}^{7+} + 5\text{Sb}^{3+} & \rightarrow 5 \text{Sb}^{5+} + 2 \text{Mn}^{2+} \\
\text{Mn}^{7+} + 5 \text{Fe}^{2+} & \rightarrow 5 \text{Fe}^{3+} + \text{Mn}^{2+}
\end{align*}
\]

Thiourea and its alkyl or phenylderivatives have been estimated in this solvent with the help of various oxidizing agents. The results obtained are within the experimental error and are reversible.

Oxidizing agents used are potassium iodate, iodine halides, potassium permanganate, potassium dichromate, potassium bromate and potassium ferricyanide. These oxidizing agents oxidize thiourea to yield thiourea formadine disulphide as:

\[
2\text{H}_2\text{N} \text{C—SH} \rightarrow \text{H}_2\text{N} \text{C—S—S—C} \text{NH}_2 + 2\text{H}^+ + 2e^-
\]

The corresponding reactions with other oxidising agents have been proposed as:

\[
\begin{align*}
6\text{RHN} \text{C—SH} + \text{IO}_3^{-} & \rightarrow 3\text{RHN} \text{C—S—S—C} \text{NHR} + 1^- + 3\text{H}_2\text{O} \\
2\text{RHN} \text{C—SH} + 2\text{I}^- & \rightarrow \text{RHN} \text{C—S—S—C} \text{NHR} + 2\text{I}^- + 2\text{H}^+ \\
6\text{RHN} \text{C—SH} + 2\text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ & \rightarrow 3\text{RHN} \text{C—S—S—C} \text{NHR} + 7\text{H}_2\text{O} + 2\text{Cr}^{3+}
\end{align*}
\]
Hydrazine has been estimated with the help of various oxidizing agents. The potential jumps near the end point are quite high. The possible redox reactions for various oxidizing agents have been proposed as:

\[
\begin{align*}
2N_2H_4 + 2I^+ &\rightarrow NH_3 + N_3H + 4H^+ + 2I^- \\
3N_2H_4 + 4MnO_4^- &\rightarrow MnO_2 + N_2 + 4OH^- + 4H_2O \\
N_2H_4 + KIO_3 &\rightarrow K^+ + I^- + N_2 + 3H_2O
\end{align*}
\]

Ascorbic acid, which is powerful reducing agent, oxidized itself to dehydron ascorbic acid as:

\[
C_6H_8O_6 \rightarrow C_6H_6O_6 + 2H^+ + 2e^-
\]

Ascorbic acid has also been estimated quantitatively with the help of various oxidising agents potentiometrically. The possible reactions could be explained as:

\[
\begin{align*}
I_2 + C_6H_8O_6 &\rightarrow C_6H_6O_6 + 2I^- + 2H^+ \\
2C_6^{3+} + 3C_6H_8O_6 &\rightarrow 2C_6^{2+} + 6H^+ + 3C_6H_6O_6 \\
2Mn^{7+} + 3C_6H_8O_6 &\rightarrow 2Mn^{4+} + 6H^+ + 3C_6H_6O_6 \\
IO_3^- + 3C_6H_8O_6 &\rightarrow I^- + 3H_2O + 3C_6H_6O_6
\end{align*}
\]

From the above observations it may be concluded that fused dibromoacetic acid is a fairly good solvent for the estimation of weak bases. Redox reactions can also be conveniently carried out in it.