Chapter 1 Introduction

Bromine is a non-metallic element occupying the third position in halogen family. A. J. Ballard[1] has discovered it in 1825 as a dark red to brown fuming liquid at room temperature (Table 1.1). Ballard observed the formation of a yellow zone above the blue color of starch, when he added the chlorine water and starch solution to the end-liquor during the manufacture of salt from seawater. On distillation of the solution reddish fumes were evolved, which on cooling and drying with calcium chloride yields liquid bromine. Ballard recognized this element and reported his discovery immediately to the French Academy of Science who suggested a name **brome** from the Greek word 'Bromos' to reflect the meaning stink. Besides Ballard, the discovery of bromine was made simultaneously by few other chemists. J. von Liebig was one among them who later failed to recognize the true nature of the new substance in time. Soon after the discovery of the new element Ballard and many others prepared the compounds of bromine, silver bromide is one, which was introduced in photography in 1840. Since then bromine became an industrially important chemical.

1.1. History of bromine

1.1.1. Occurance and properties of bromine. Bromine exists commonly in the form of salts, which are found in the sea, rivers, lakes and under ground waters along with the most abundantly available chloride salts (Table 1.2). However, most of the earth's bromine is believed to be concentrated in the hydrosphere. The concentration of bromine in ocean water is about 65 mg per liter[1] and varies in parallel with the concentration of other salts. Saline is the another source of bromine, one such is found at Kharaghoda, near to the river Indus in India which is also called the *Rann of Kutch* and is spread over an area of about 18,000 Km^2. The bromine containing wells are usually found in the United States[1], mainly in the states of Michigan, Ohio and West Virginia. The well-brines are usually natural but in many cases they have been created by pumping water into the salt layers which lie hundreds of meters below the surface. The greater part of bromine salts estimated to be 10^{15}–10^{16} tons occurs in the form of rocks in the earth crust. Bischoffite, $MgCl_2.6H_2O$ and tachhydrite $CaCl_2.2MgCl_2.12H_2O$ are among the main minerals richest in bromine (0.44 - 0.47%) (Table 1.3).

Table 1.1. Physical properties of bromine

Physical property	Nature/Value
Appearance	Highly dense fuming dark red lacrimatory liquid
Odour	Strongly pungent
Colour	Yellow orange at 20 K; Red brown-orange red-almost black at melting point; Dark red liquid <59 °C; Orange to red brown vapor >59 °C.
Density	3.12 at 20°C
Boiling point	58.8 °C
Freezing point	-7.3 °C

1.1.2. Recovery of bromine. Bromine is obtained by the oxidation of bromide salts. It can be affected by chemical or electrochemical method. The sea or under ground brine or bittern from salt industry or the effluents wherein the bromide concentration varies from 0.065 to 12 g/l, are largely used as the source for bromine recovery (Table 1.1). In chemical methods[1], oxidizing agents such as elemental chlorine or oxo-compounds like MnO_2 or salts like BrO_3^- and ClO_3^- are useful. Oxidation of bromide with the oxo-compounds involves always a mineral acid. A. Frank[1], for the first time, reported the extraction process by the oxidation of bromide using MnO_2 in sulfuric acid medium at 60°C. This process was uneconomical because it was a batch type giving low yields of bromine. Later, the chlorate[2], ClO_3^- was used in place of MnO_2. The necessity to add mineral acids like H_2SO_4 or HCl along with the oxo-compounds was the main limitation with these methods because of their high cost and handling difficulties faced in their transportation. Moreover, the precipitation of calcium as calcium sulfate may lead to clogging the parts of the equipment whenever the low cost H_2SO_4 was used. Later on, the above method was made continuous by using chlorine as an oxidizing agent[3] The problems normally faced in this method are the handling of the more corrosive chlorine gas, the difficulty in transporting of it and the too small local demand for bromine.

Therefore, the use of oxo-compounds in the bromine recovery is thus justified. Yet, chlorine has the advantage of being a co-product of chlor-alkali industry. Electrochemical methods are based on the principle that bromide undergoes oxidation by one-electron per atom at suitable anode materials. This is possible even in the presence of large concentrations of chloride due to the fact that the decomposition of bromide is lower by 0.29 V (the standard oxidation potentials of chloride and bromide are +1.356 V and +1.065 V, respectively). Electrochemical methods for the oxidation of bromide solution are low intensive in energy and thus more economic than using chlorine by chemical method. However, the electrolytic method of oxidation of bromide in the bromine recovery has not yet been proved superior than the chemical methods. This could be due to low concentration of bromine in the source, deposition of magnesium hydroxide and the presence of sulfates. The two electrochemical methods that were tried in Germany are Wunsche process[4] and the Kossuth process.[5] The former process uses a two compartment cell having anode and cathode made up of graphite. A porous clay was used as a

Table 1.2. The occurrences of bromine

Source	Original content, g/L	After concentration, g/L
Sea water	0.065	
Inland seas		
Kharaghoda, Indian Ocean	0.25	6
Sassyksee, Black Sea	0.28	1.5 to 4.5
Shebhka el Melah, Tunisia	2.50	6.8
Salt lakes		12 to 13
Dead Sea, Israel	4 to 6	
Ellon Sea, USSR	0.63 to 2.25	
Searles Lake, Calif (USA)	0.85	
Brine wells		
Michigan (USA)	2 to 3	
Arkansas (USA)	4 to 5	
Yakutsk, Siberia, USSR	6 to 7 ($CaCl_2$ solution)	

Table 1.3. Some important bromine deposits in earth crust

Mineral salt deposits	% (w/w)
Tachydrite ($CaCl_2.2MgCl_2.12H_2O$)	0.438
Rock salt	0.005 to 0.040
Sylvite	0.117 to 0.300
Carnallite	0.155 to 0.0334
Bischofit ($MgCl_2.6H_2O$)	0.467
Hard salt	0.05 to 0.20

diaphragm between the electrodes for better current efficiency. One of the main disadvantages of this process is clogging of the pores of the clay diaphragms by the magnesium hydroxide that was caused by the hydroxyl ions produced in the cathode compartment. The second process was a simple cell having bipolar carbon electrodes without any diaphragm in between. The magnesium hydroxide precipitated on the cathode was dislodged by reversing the polarity of the electrodes and subsequently removed from the brominated solution by filtration before it was sent to stripping column. Although, this process is advantageous over the above Wunsche process in overcoming the detrimental effect of magnesium hydroxide precipitation on the diaphragm, it is inferior due to low current (40 – 50%) efficiency.

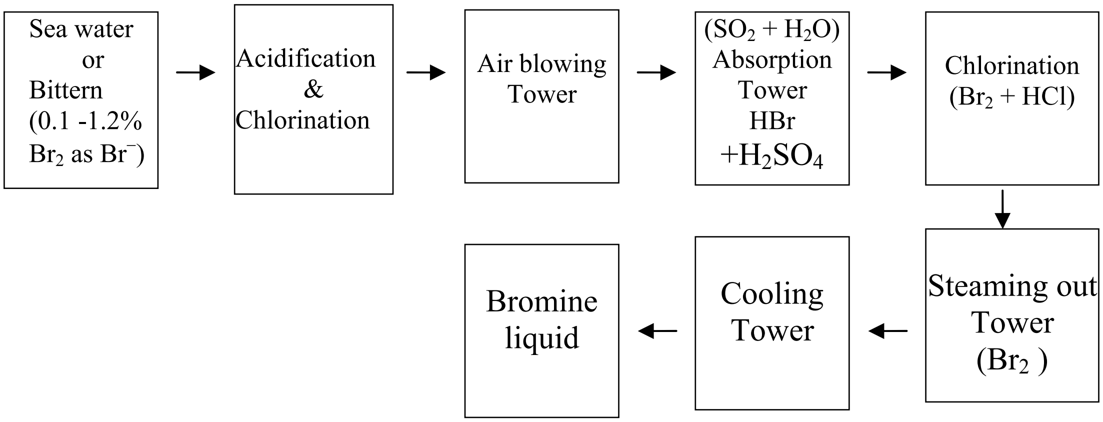
More recently, the continuous manufacture of bromine and its steam distillation was described.[6] The aqueous solutions of bromides like HBr and NaBr were oxidized with chlorine. T. Jakagi[7] *et al.* reported the concentration and manufacture of bromine by ion exchanger electrolysis. In this method, a saturated solution of bromide containing raw salt was prepared and electrolyzed in an anode chamber of an ion-exchanger type cell under a slight application of pressure to concentrate bromine in the returned salt water. The bromine coming along with the chlorine was separated by an evaporation or air-blowing method. N. Ogawa[8] *et al.* patented the manufacture of bromine by the oxidation of bromide in bromine containing salt solutions with chlorine gas at $pH \leq 4$ and the freed bromine was separated with air in packed columns.

A catalytic process for producing bromine from inorganic bromides was patented by P. Schubert[9] *et al.* This process requires to acidify the source material to produce a gaseous hydrobromic acid which produces a stream of bromine and water vapor upon mixing it with oxygen over a catalyst. R. C. Williams[10] *et al.* described an automatically operated electrolytic cell assembly and a method of efficiently providing brominated water for swimming pools and for other similar applications. Bipolar graphite electrodes with the mechanism to power on and off at a selected time between 1– 60 s and to reverse the polarity of the electrodes for about 5 s to clean the electrodes were provided here to stop the formation of hydrolyzed products. A process on bromine extraction from sea water was patented by R. Khamizov *et al.*[11] However, the concentration of bromide in the eluate reaches to ≥ 5 g/l, this processes requires large quantities of strongly basic anionic exchanger for bromide ion sorption and desorption at 50 – 95 °C, and its regeneration. M. Jean-Charles[12] *et al.* reported a combustion and high temperature-high pressure apparatus for bromine recovery from liquid effluents. The combustion gases were cooled and subjected to hetero-azeotropic distillation to obtain the gaseous water-bromine mixture. The bromine was decanted at around 5 °C and distilled to get the purity of 99.9%. M. Yamada[13] *et al.* processed the photographic wastewaters for the recovery of bromine. It comprises the separation and recovery of bromine by spray incineration of photographic waste water with alkali metal hydroxides, carbonate salts, nitrate salts and/or organic acid salts under oxidation atmosphere. Chlorine gas or hypochlorous acid were used to free the bromine in the incinerated water solution.

However, the bromine is still recovered by two industrial processes called as (i) Steaming out process (ii) Air blowing process.

Steaming out process. This process involves first acidification of seawater or bittern by mineral acids and then the oxidation of bromide to bromine by chlorine. The aqueous mixture containing bromine and chlorine steamed out by hot air and then followed by liberating the bromine vapors by the acidification and condensing the vapors cooling towers. Finally pure bromine was obtained by the distillation.

$$
\begin{aligned}
2\,Br^- + Cl_2 &\rightarrow Br_2 + 2\,Cl^- \\
Br_2 + SO_2 + 2\,H_2O &\rightarrow 2\,HBr + H_2SO_4 \\
2\,HBr + Cl_2 &\rightarrow Br_2 + 2\,HCl
\end{aligned}
$$

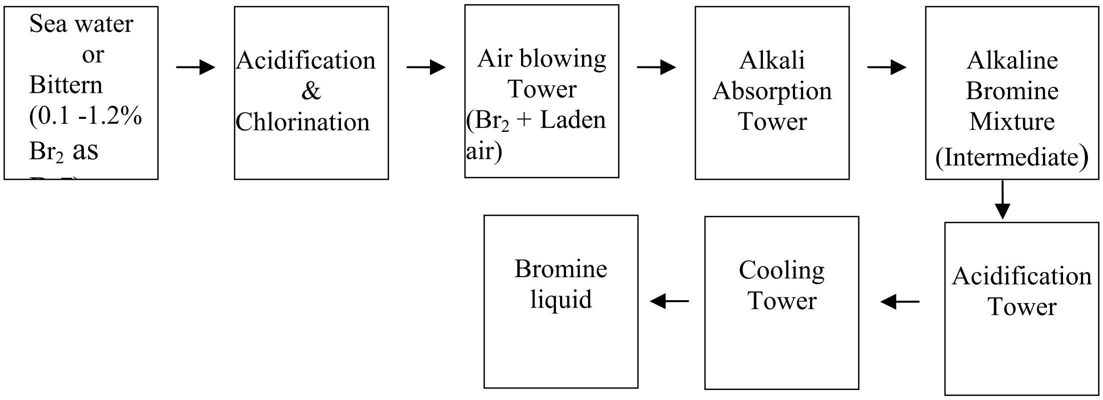


Air blowing or alkali absorption process. In this process also follows the first two steps of acidification and oxidation of seawater or bittern to liberate the aqueous bromine as in the case of steaming out process. The aqueous bromine will be made absorbed in the alkali to form the mixture of bromide and bromate. The acidification of bromide and bromate, the liberated bromine was cooled and collected as pure liquid bromine.

$$2\,Br^- + Cl_2 \rightarrow Br_2 + 2\,Cl^-$$

$$3\,Br_2 + 6OH^- \rightarrow 5\,Br^- + BrO_3^- + 3\,H_2O$$

$$5\,Br^- + BrO_3^- + 6H^+ \rightarrow 3\,Br_2 + 3\,H_2O$$



The first economically successful recovery of bromine directly from the sea was carried out near Wilmington, North Carolina (USA), using an air-blowing process originally developed for brine operations by H.H. Dow, USA.

The use of air rather than steam has been preferred, because the cost of steam to heat ocean water, with its bromine content of only about 65 mg/litre. would be prohibitive. Another process for the recovery of Bromine from sea water was developed on a commercial scale by Ethyl Corporation in the US. The process involved the treatment of seawater with chlorine and aniline and collection of the precipitated Tri bromo aniline.

1.2. Global scenario of bromine

Present Global demand for bromine is estimated to be around 5,00,000 tonnes per year. The annual growth rate in demand is estimated to be around 3% per year. United States is the major world producer of bromine, followed by Israel. Israel has been able to increase its production substantially from 23,000 tonnes in 1976 to around 2,00,000 tonnes per annum at present, due to the availability of (Dead Sea Brine and its concentrates) the richest source of bromine and the innovations brought in the process by various technologists.

1.3. Global outlook of bromine

Recovery of bromine form seawater is mainly done in US, erstwhile USSR, Italy and Japan. Phasing out of methyl bromide and ethylene bromide has forced bromine production to diversify into new markets. Still, the largest end-use for bromine compounds, flame-retardants accounts for 30% of world bromine consumption. About 45% of this is consumed in US, 31% in Western Europe and 14% in Japan. Aside from flame retardants, several major producers are developing their fine chemicals capabilities for bromine to meet the demand from the pharmaceutical industry. During the mid-1990s, a number of anti-hypertension drugs were introduced using bromotoluene as an intermediate in the manufacture. Another intermediate, bromo-methoxy naphthalene, is important in making naproxen, an anti-inflammatory that came off-patent in 1997. Other promising new sectors for bromine include swimming pool disinfectants, industrial water treatment, air conditioning absorption systems and precious metal leaching.

According to the survey conducted in the year 1993, the total world's annual production of bromine was estimated to be about 5 lakh tons. About 47% of this had been consumed in the production of fire retardants. TBBPA and tetrabromo diphenyl ether are being used worldwide as potential fire retardants. Considering that 20% of total world's bromine production goes into the manufacture of these compounds, then their production has been estimated to be around 0.60 lakh tons annually.

1.4. National status of bromine

The bromine production during 1995-2000 in India was found to be around 2000-2200 tons in addition to the 500-750 tons of imported material. CSMCRI is pioneer in the research field and carried out developmental studies on the recovery of bromine from Indian sea brines. The institute has developed a steaming out process for the recovery of bromine from end liquor (bittern) of salt industry in early seventies and has released know how to few entrepreneurs in the country. Before 1970, bromine production of the country was less than 400 tons. This has increased to about 2,200 tons annually mainly because of increase in the number of bromine producing plants installed based on CSMCRI know how.

1.5. Industrial importance of bromine

Soon after the discovery of bromine, the reactions of it with various organic compounds were studied at length. Since then, the bromine has become as an important reagent in the field of chemistry. It was later found useful extensively in the field of medicinal chemistry and photography. The use of silver bromide was first introduced in 1840 in photography, which made the bromine to recognize as an industrially important chemical. The requirement of silver bromide had slowly increased with the gradual developments in the fields of photography, advent of film, motion pictures and X – ray photography that paved the way for the rapid extension of the use of bromine. The use of bromine in medicinal chemistry had begun almost as early as in photography. This was slow in early days, but spread later over the developed countries of Central and West Europe and North America. The compounds of bromine are well represented in many other areas such as gasoline additives, agricultural chemicals, flame retardants, dyes, pharmaceuticals etc (Table 1.4). Besides, the high-density organo bromine compounds are known to be useful as hydraulic, gear/ore flotation fluids, the $CaBr_2$-$ZnBr_2$ composition as drilling fluid and the 1,2-dibromo ethylene as anti-knocking agent in gasoline. In addition, bromine is directly used as disinfectant in swimming pools, and as anti oxidant to control the growth of bacteria, algae and odor in cooling waters. It is also used for desizing of cotton, bleaching of pulp and paper, and in laboratories as a reagent.

Bromine is found in living organisms but its biological role is unknown. Many investigations concerning the bromine content of plants and animals, especially of the human body have been made. So far no physiological significance of bromine has been proved. There are two bromine compounds found in marine organisms. Dibromotyrosine was found in coals, algae and sponges. Dibromoindigo– a well known Tyrian purple dye was found in the bodies of two species of snails, *Murex brandaris* and *Murex purpureus*.

1.5.1. Industrial Organic intermediates. The commercial importance of organic compounds of bromine with their chlorine analogues arises mainly due to the certain offered advantages of physical or chemical properties. The use of organobromine intermediates is small as compared to their use as end products. A large number of bromine compounds have commercial value in both industrial use as well as in laboratory purpose.

Table 1.4. Applications of some industrially important organobromine compounds.

Bromocompounds	**Applications**
Bromine	Manufacture of pharmaceuticals, organic preparations, dyes, pesticides, fire retardants, germicides, photographic chemicals, perfumes, heavy brines and other chemicals
Allyl bromide	Organic synthesis
Ethyl bromide	Organic synthesis, Used in the manufacture of Pharmaceutical like Vitamin A etc., in flame-retardants, refrigerant
Bromochloromethane	chemical intermediate, solvent, pesticide chemical, flotation agent
Methyl Bromide	As fumigant for soil fumigation and for space fumigation to control insects in stored products
Ethylene di bromide	As fumigant and an important constituent of Ethyl petrol used as a motor fuel. Ethylene dibromide finds use as an agricultural fumigant but this use in the United States is now prohibited because of ground water
N-Butyl Bromide	Intermediate for Pharmaceuticals, Insecticides, Quaternary Ammonium Compounds and Pigments.
Isopropyl Bromide/ N-propyl bromide	Intermediate for Pharmaceuticals, Insecticides, Quaternary Ammonium Compounds, Flavors and fragrances
Isobutyl bromide	Organic synthesis, pharmaceutical intermediates
Bromobenzene	Solvent, organic synthesis, agricultural intermediates, pharmaceutical intermediates
Bromoform	Agricultural intermediates, polymerization agent, ore selecting agent
Cetylbromide	Organic synthesis, surfactant manufacturing, imaging chemicals
Propyl bromide	solvent, organic synthesis, pharmaceutical intermediates
Bronopol/2-bromo-2-nitro-1,3-propane diol	In cosmetics as a bactericide, antiseptic and preservative. Preservatives for coatings, slurries and to control microbial fouling in paper mills and process water systems
2,4,6-Tribromophenol	Intermediate for high molecular weight flame retardant. Effective fungicide and wood preservative
2,4,4,6-Tetrabromo-2,5-cyclohexadienone	As selective brominating reagent and as many functional group transformation in organic synthesis
Tetrabromobisphenol-A	Solaris FR10 is highly effective when reacted into epoxy resin system, due to its structural compatibility, high bromine content and thermal stability Its high purity allows its use as a reactive flame retardant for polycarbonates and as an additive for styrenic thermoplastics such as ABS and HIPS
4-Bromoanisole	Organic Synthesis, Pharmaceutical Intermediates
1-Bromo-2-naphthol	In organic synthesis
1,6-Dibromo-2-naphthol	In organic synthesis
6-Dibromo-2-naphthol	In organic synthesis

Bromocompounds	**Applications**
2,4,6-Tribromoaniline	Industrial intermediate
4-BromoN, N-dimethyl aniline	As dye intermediate
4,6-Dibromo-2-nitro aniline	Dye intermediate and in organic synthesis
2,6-Dibromo-4-nitro aniline	Dye intermediate and in organic synthesis
4-Bromoacetanilide	Drug intermediate in pharmaceutical industry
N-Bromosuccinimide	As a secondary brominating reagent and also as functional group transformation
Benzyl bromide	In organic synthesis, as a solvent
4-Nitro benzyl bromide	Intermediate in organic synthesis
1-Bromonaphthalene	Organic synthesis
1,2-Dibromocyclo-hexane	Intermediate in organic synthesis
1,2-Dibromocycloocane	Intermediate in organic synthesis
Styrene dibromide (α,β dibromostyrene)	In polymer chemistry, drug intermediates
α,β Dibromo-4-methyl styrene	Inorganic synthesis
1,2-Dibromohexane	Inorganic synthesis, as solvent
1,2-Dibromooctane	Inorganic synthesis, as solvent
2,3-Dibromo-1-propanol	Organic synthesis
α,β-Dibromochalcone (Chalconedibromide):	Drug intermediate, Organic synthesis
2-Bromocyclohexanol	Chiral intermediate in organic synthesis, as solvent
1-Bromo-2-phenylethanol	Chiral intermediate in organic synthesis
1-Bromo-2-(4-methyl phenyl)ethanol	Organic synthesis
α-Bromo-β-hydroxy styrene	Intermediate in cosmetic industry, polymer chemistry
1-Bromo-2- hexanol & 2-bromo-1-hexanol	Organic synthesis, as solvent
1-Bromo-2-octanol & 2-bromo-1-octanol	Organic synthesis, as solvent

A large variety of brominated compounds are usually prepared with the help of liquid bromine through addition or substitution reactions. They largely include commercially important products such as: tetrabromobisphenol-A (TBBPA)—a flame retardant, which is used as an intermediate in the preparation of epoxy resins. TBBPA is the largest volume brominated flame retardant. It is used as both an additive and as reactive flame retardant. It is used as an additive in ABS (acrylonitrilebutylstyrene) preparations in large volume because of its relatively low cost and most effective flame retardant. In ABS, TBBPA provides the high flow and good impact properties. It is more stable towards UV light. Eosin is another important pigment used in personal care products such as lipsticks, nail paints and also as pigment in many pharmaceutical products. Bromoacetanilide is an analgesic and antipyretic agent and as intermediate in drug industries. Tribromophenol is an intermediate used in the manufacture of antiseptic, germicide, fungicide, fire extinguishing fluids, and fire retardant. 2-Bromo-4-nitro acetanilide- a drug intermediate used in the preparation of nimenslide. Vinyl bromide is used in manufacturing bromopolymers mainly polyvinyl bromide. It is used as a flame retardent in acrylic fibers. It is used as an alkylating agent in the synthesis of organic compounds (pharmaceuticals, fumigants, leather products). Vinyl bromide is also used in polymerization and copolymerization of plastics, metal fabrication industries and lamination of fibers. Some other important industrial intermediates, methyl bromide, 1,2-dibromoethane, bromobenzene, dibromobenzene, styrenedibromide and other alkyl bromides and aromatic bromo compounds are widely used as solvent and as well as in the preparation of Grignard reagents. Bromobenzene is used as a starting material in several organic syntheses,[14-17] especially in the preparation of organometallic reagents such as phenyl magnesium bromide,[18-26] phenyl lithium,[27,28] diphenyl disellinide.[29] Bromobenzene is widely used as an additive in motor oils and as a heavy liquid solvent especially where mass crystallization is required.[30] It is further used for the preparation of diphenyl zinc which in turn are employed in the preparative synthesis involving carbon-carbon bond formations.

2,4,4,6-Tetrabromo-2,5-cyclohexadienone is found to have wide applications in synthetic organic chemistry. It is used in the preparation of linear poly (phenyleneoxides),[31] direct monobromination of imidazoles and N-methylindoles,[32] in selective monobromination of aromatic for the preparation of α,β-unsaturated bromoketones,[33-36] for the preparation of brominated algal components *via* bromination of myrcene,[37] for the direct brominative ring closure,[38] for the synthesis of carbocyclic molecules,[39] in a stereo-controlled synthesis of disubstituted tetrahydrofurans,[40] for the oxidative synthesis of disulphides,[41] in the synthesis of 6-bromocamphene and 9-bromolongifolene,[42] as reagent combination for converting the alcohols to azides,[43] silylethers to alkylbromides,[44] tetrahydropyranylethers to alkylbromides,[45] for allylic bromination of β-lactam antibiotics[46] and in several other total syntheses.[47-55]

N-Bromosuccinimide (NBS) is an important reagent useful for multiple applications in synthetic organic chemistry. NBS is used as a secondary brominating reagent in bromination of allylic compounds,[56-58] bromination and simultaneous decarboxylation of terminal olefins,[59] bromination of carboxylic acids and acetylinic bromination of steroids.[60] NBS is further known to be used as dehydrogenating reagent[61] or for the selective oxidation of secondary alcohols to the corresponding carbonyl compounds.[62] The selective debromination of 1,6-dibromo-2-naphthol at C_1–position to give 6-bromo–2–naphthol in the presence of various catalytic media have been reported.[63] Further, 6-bromo-2-naphthol has been used as coupling intermediate in many synthetic reactions/applications.[64,65]

1.5.2. Dyestuffs and dye intermediates. The introduction of halogen atom substitution in dyes and dyestuff molecules has a marked effects on physical properties and thus beneficial to dye industry. The introduction of bromine in a dyestuff molecule often produce a desirable/remarkable change in the color shade, usually more marked than the corresponding chloro-compound. The other possible physico-chemical changes occur on the substitution of one or more halogen atoms in dyestuffs are likely to be their solubility, reactivity, stability, molecular weight, melting/boiling point, tinctorial value, etc. Bromine substituted intermediates are used in many instances with the bromine playing an essential part either when contained in the final dyestuff or as a reactive site. The dyestuff are classified as *Anthraquinone dyes, Indigoids and thioindogoid dyes*, *Azo dyes, Phthalocyanine pigments and Phthalein and other dyes.*

Anthraquinone dyes. They are bromoanthraquinone and its derivatives which are frequently used as intermediates, readily prepared and equally important. The reactivity of the bromine when it is at α– or C_1– carbon is more suitable for further replacement reactions. Nuclear bromination of polycyclic anthraquinone compounds often improve the tinctorial strength and the light fastness.

Indigoids and thioindogoid dyes. The introduction of bromine into indigoid dyes leads to products of brighter shades and an improved affinity for the fibres when used as a vat dye. Tetrabromoderivative of indigo gives very good affinity to dye the fabric.

Azo dyes. The introduction of bromine into azo dyestuff can often be justified in highly polar monoazo blue and violet dyes. The bromine containing coupling-components are used in azoic dyes (azo dyes formed within the fibre) to give deep shades.

Phthalocyanine pigments. Green pigments particularly valuable in paints and inks are resulted from the highly brominated/chlorinated blue-derivatives of copper-phthalocyanine.

Phthalein and other dyes. Fluorescein is the parent dyestuff of its class but its tetrabromo-derivative, Eosine is of greater commercial importance. Eosine is being isolated as a sodium salt used in textiles, paper dying, in the manufacture of inks and in the purified form for the coloration of drugs and cosmetics. It is also used as an indicator.

1.5.3. Medicinal Chemicals. The effect of bromine substitution in many medicinal products is vital but it is impossible to generalize about its functions. Many active drugs are bromine contain substituted products. The manufacture of many other medicinal products relay on brominated intermediates. One example is the general halothane anesthetic which contain a single bromine atom in its chemical structure. Naproxen, a new analgesic, utilizes a brominated intermediate in its manufacture. The antihistamine, bromopheniramine maleate, and the cough medicine dextromethorphan hydrobromide, also utilize bromine in their preparation. 1-Bromogalanthamine is being developed for potential use in treating Alzheimer's disease. Bromhexine has improved the performance of amoxicillin in the treatment of pneumonia. Bromocriptine is effective in the treatment of cocaine addiction. Many of the commonly used sedatives, antihistamines and antitussives can be made at a lower cost thanks. Some of the new anti-cancer drugs are being made using bromine.

Quaternary ammonium bromide is used as germicides. The quaternary ammonium bromide containing a long chain aliphatic residue attached to the quaternary nitrogen atom, evolved over many years as the anti-bacterial properties of several cationic dyestuffs. Many other related quaternary ammonium bromides have been used as autonomic drugs. Dibromopropamidine is used as an antiseptic usually in the form of ointment or cream. It has antibacterial and fungi static properties and thus finds wide application. Bromopheniramine maleate is a potent antihistaminic agent with a low incidence of side-effects. Halothene (Fluthane) represents a major advance in anaesthetics. It is being used increasingly throughout the world as it fulfills most of the requirements of perfect anesthetic. Ethylbromide has been used as a narcotic and as an anesthetic. p-Bromoacetanilide is used as an analgesic or intermediate in synthetic organic chemistry. Tribromophenol is used as an antiseptic, a starting material for the preparation of 2,4,4,6-Tetrabromo-2,5-cyclohexadienone or an intermediate in the coupling reactions. The bromine substituted aromatic compounds are used as intermediates in many pharmaceutical industries.

1.5.4. Disinfectant chemicals. Disinfectant is an agent applied to inanimate objects to destroy, neutralize, or inhibit the growth of disease-carrying microorganisms, whereas antiseptics are applied primarily to living things. Wood & Illing[66] and Beckwith & Moser[67] have investigated germicidal activity of bromine. The former[66] showed that 0.15 ppm bromine kills the *Escherichia coli* suspended in water within five minutes. The latter workers[67] showed bromine as more effective germicidal agent than that of chlorine and iodine for killing both *E. Coli* and soil bacteria in tap water. The use of bromine for disinfections of swimming pools was pioneered in the early years. The bromine is more popular because of its less odor as compared to that of chlorine. The additional advantages of bromine being used as a disinfectant of swimming pools has been pointed out.[68] In presence of nitrogenous matter from bathing load, bromamines are formed, which were found to be effective bactericidal compounds. A mixture of an aqueous bromine solution and bromine stabilizer has been used to generate stable oxidizing bromine compounds for use as a biocide.[69] The stable biocide formulations containing oxidizing bromine are provided for befouling control in industrial water systems.

1.5.5. Agricultural chemicals. The use of bromine compounds in agriculture has been relatively gone up due to the development of modern agricultural science and pest control. In the agriculture field, the pest control is major problem in the world and need to be rectified by the use of pesticides and insecticides. At the same time bromine has been stimulated by the chemical industries for other purposes. The most commonly used bromo compounds in agriculture are methyl bromide, ethylene dibromide and dibromochloropropane. Methyl bromide and ethylene dibromide have been used as space fumigates and soil fumigants. The insecticidal properties of ethylene dibromide were first described in 1925, and its use as a grain fumigant was reported in 1946.[70,71] Both methylbromide and ethyl bromide are used widely for the fumigation of fresh fruits and vegetables. Ethylene dibromide has also been used to fumigate fresh fruit and vegetables against various stages of certain fruit flies. Methyl bromide has outstanding penetrating properties this has made it popular in the fumigation of seeds. Methyl bromide and ethylene dibromide are commonly used as space fumigants. Dibrom (1,2-dibromo-2,2-dichloroethyl dimethyl phosphate) has wide spectrum of pest control and hence it is extensively used as pest control. Dibrom has a minor use as a space fumigant in tobacco warehouses and green houses. Methyl bromide has also been used in a number of ways to control various plant viruses–tobacco etch and necrosis, cucumber necrosis and mosaic, tomato ring spot, tobacco mosaic, and sugar cane mosaic. Bromoxynil (3,5-dibromo-4-hydroxybenzonitrile) is extensively used as herbicide.

1.5.6. Mining chemicals. Bromine is one of the few common elements conferring high specific gravity to the compounds containing it and therefore, it has been used extensively in the preparation of heavy liquids. These heavy liquids especially used for many years in the mineralogical laboratories and mineral processing plants for quantitative separation of ores into their constituent minerals based on differences in the specific gravity and identification of mineral ores. The separation of solid particles by differences in specific gravity is used for analytical purposes mainly in mineralogical and petrographical laboratories.

1.5.7. Polymeric Compounds. Numerous plastics and rubbers contain halogen atoms as a normal constituent of their primary structure. Some of the halo-polymers like poly-vinyl chloride (PVC), poly-vinylidene chloride (Saran), poly-tetrafluorethylene (Teflon), etc have achieved importance in the plastic industry. The bromine-containing polymers are also important because of high reactivity of bromine and the stability of bromopolymers. Bromopolymers were found to be very useful models in the structural studies. The physical chemists found that the heavy bromine atom is a convenient marker in the X-ray analysis of polymeric systems and in the optical study of macromolecular solutions. Some of aliphatic bromo-polymers are highly unstable due to high reactivity of bromine atom and for their ready decomposition under the influence of physical or chemical agents. Recently, synthetic bromo-polymers and bromine modified natural polymers rose to prominence as fire-resistant compounds. Among the aliphatic bromo-polymers, poly-vinyl bromide is an important bromopolymer. Polyvinyl bromide is an important macromolecule in the polymer chemistry and finds many applications. The aromatic bromo-polymers like poly-bromostyrene plays most important role. Most of the poly-bromostyrenes are transparent colorless materials having good mechanical, thermal and electrical properties. The relative stability of bromo-polystyrenes has not only made the bromostyrenes interesting starting materials for the synthesis of other polymeric materials but has also attracted some attention to their use as co-monomers. Vinyl bromide is one of the important monomer of macromolecular chemistry. Vinyl bromide is used in manufacturing bromopolymers mainly polyvinyl bromide. It is used as a flame retardent in acrylic fibers. It is used as an alkylating agent in the synthesis of organic compounds like pharmaceuticals, fumigants, leather products. It is used in polymerization and co-polymerization of plastics, metal fabrication industries and lamination of fibers. Vinyl bromide will undergo both homo polymerization and co-polymerization with methylmethacrylate and styrene to give macromolecule. The copolymers of vinyl bromide with methylmethacrylate and styrene were used in their radiochemical studies. Bromoprene is another monomer which can undergo homo-polymerization to give poly-bromoprene which is good elastomer (synthetic rubber). Bromopolymers may lead to the formation of self-extinguishing polymers with good fire resistance. Since, the flammability of organic plastics has been a deterrent to their wider acceptance in many applications. The major efforts made by the producers were either to find suitable brominated additives for the regular plastics or to develop new bromine-containing polymers.

1.5.8. Fire-extinguishing chemicals. Bromine containing fire-extinguishing agents will be used in different occasions. The fire involves the burning of solids such as wood, papers, plastics etc, or burning of liquids and or fire associated with electricity. Some are excellent vaporizing liquid flame-extinguishing agents used in commercial fire and explosion suppression systems. Some have been used in combination with an inert siliceous powder to extinguish fires on liquid chlorosilanes. This system is superior to other extinguishers because it does not evolve the toxic gases that are generated when water or conventional carbonate extinguishers are used. Bromine containing compounds methyl bromide, bromochloromethane were found to be effective advantages. Bromochloromethane was developed commercially in Germany during World War II. Bromochloromethane was used extensively by German armed forces and it was found to be more effective than carbon tetrachloride. Carbon tetrachloride has also been used as extinguishing agent, but it is quite toxic as compared to bromine extinguishing agents. Following the World War II, considerable efforts were made to develop flame extinguishing compounds with improved properties of toxicity and stability. The bromo compounds of fire-extinguishing property include hydrogen bromide, dibromomethane, bromodifluoromethane, bromotrifluoromethane, bromochlorodifluoromethane, etc.

1.5.9. Flame retardant chemicals. Bromine is used as the building block for some of the most effective flame-retarding agents available to the plastics industry today. They are used to protect against the risk of accidental fire in computers, televisions, radios, stereo systems, video players, and in products made of textiles and wood. Brominated flame-retardants also are used to improve the fire safety of foam padding used in upholstered furniture, in the plastic coating on electrical wire, and even in carpeting. Brominated flame-retardants, as all flame-retardants act to decrease the risk of fire by reducing the risk that an object will ignite. Many objects of daily used are mixed with flame retardants while in their fabrication so that common occurrences such as TV or computer being left on all night and overheating, an electrical short circuit taking place in electronic devices or cigarettes accidentally dropping on a sofa or curtain do not result in a fire.

In addition to reducing the likelihood that an item will ignite, flame-retardants hinder the spread of the fire, and provide valuable extra time in the early stages of a fire when it is much easier to escape. A room fire can very quickly escalate to the point where enough heat is generated that all combustible material in the room bursts into flames. This situation is known as "flash-over" and can occur in a matter of minutes from ignition. Flame-retardants slow down the initial burn rate and thereby can help increase the time to flashover, giving the occupant more time to escape.

Reducing the flammability of various flammable solid materials is another important application of bromine compounds. Tetrabromobisphenol-A, is an important fire retarding agent being widely used successfully. Its structure provides a product satisfying the properties desirable in a commercially acceptable flame retardant epoxy resin. The resins are used in coatings, castings, laminates, adhesives and other miscellaneous applications where flame retardancy is highly desirable.

All of these fire-extinguishing and flame retardant materials contain bromine bound into an organic molecular structure, that is, one based on a framework of carbon and hydrogen atoms. Bromine functions as a flame retardant by interfering with combustion at some stage in the process, i.e. during heating, ignition or flame spread. The actual mechanism of retardancy is not fully understood, but it is believed that bromine acts primarily by removing high energy oxygen and hydrogen radicals that are formed during the combustion process.

1.5.10. Photography chemicals. Bromine compounds have a number of applications in photography. Several compounds are used to make the all-important light-sensitive component of a photographic emulsion, without these bromine compounds your pictures will not capture the light. Other bromine compounds are used as an ingredient in photo developing solutions- without which the pictures wouldn't be developed. Silver bromide possesses the best properties for the production of highly sensitive photographic materials.

1.5.11. Other chemicals. Bromine compounds are being tested in new batteries for electric vehicles designed to have zero emissions. This potential market for bromine compounds may have a big positive impact on our environment. Many solvent users are switching from chlorinated solvents to brominated solvents because of the need for less toxic cleaning solvents to increase workers safety, concern about ozone depletion issues and the need to reduce volatile organic emissions (VOEs). Brominated solvents are excellent options for users who want to obtain optimal cleaning performance and low-to-no flammability.

1.6. Hazardous of Bromine

Acute exposure of liquid bromine may cause burns of the skin, mouth, throat and stomach.[72] Brown discoloration and corrosion of the tongue and mucous membranes, sore throat, giddiness, vomiting, and abdominal spasm may occur. Severe gastroenteritis with possible ulceration or perforation, prostration and circulatory collapse may also occur. Dilute solutions may also cause fatal gastroenteritis.

The handling of liquid bromine requires the personal protective equipment[73] (PPE). Some of the PPEs are respirators, safety goggles, gloves, aprons and boots. The PPE recommendations include both normal use and emergency response during a fire, spill, leak, or accidental release.

The green–bromine or new brominating agent, HOBr is assumed to react with organic substrates with high yields and maximum bromine atom efficiency (95-100%). Besides, it will have many advantages over liquid bromine. It is easy to handle, transport and does not require special equipment or care in its applications. Moreover, it is very stable on storage and can replace corrosive liquid bromine in bromination reactions. It can be prepared inexpensively from the intermediate mixture from bromine recovery plants by cold process.

1.7. Objectives of the present work

From the literature search, it revealed that there is no substitute for highly volatile corrosive liquid bromine in many of its organic reactions. It is therefore, propose to develop a bromine substitute based on bromide-bromate combination using the alkaline bromine mixture, an industrial intermediate in one of the bromine recovery processes and to develop systematic techniques required to it. The objectives and scope of the present work are described as under.

- To investigate the effects of sulfuric acid as well as chloride, bromide and bromate ions on the absorption spectra of aqueous-bromine.
- To develop a rapid, simple, sensitive and accurate method for the determination of bromide in excess bromate while bromate in excess bromide in the presence and the absence of excess chloride in H_2SO_4 medium. Application of these methods in the determination of bromide present in industrial mixture, debrominated

effluents, sea water, brine, bittern, soil samples and plant extracts while bromate in industrial mixture, and debrominated effluents.

- To develop non-solid brominating reagents so as to carry out some of the substitution and addition reactions bromine with various organic substrates by non-hazardous ways by utilizing industrial alkaline bromine mixtures.
- To investiagate spectrophotometrically the formation of hypobromous acid HOBr from bromate–bromide salts and study the kinetic of formation and decomposition of HOBr.
- To carry out the bromination by eco-friendly methods using solid brominating reagent through i) substitution mechanism with various organic substrates such as phenols, amines, amides/imides, ethers, hydrocarbons etc and ii) addition reactions involving olefins.
- To conduct further the selective dehalogenation reactions of poly halophenols and naphthols using H-β-zeolite and a mixture of sulfite and bisulfate.

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