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Review on Surfactants, Preparation and Their Applications and The Ionic Liquid Base Surfactants as Next Gen

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ABSTRACT:

Introduction: The evolution of industries and technology across various sectors, including chemical, petrochemical, agrochemical, pharmaceuticals, and cosmetics, has been accompanied by continuous advances in science and technology over time. These advancements have utilized natural resources such as fossil fuels, hydrocarbons, and crude oil, contributing to economic growth and improving convenience in our daily lives. However, these developments have also led to detrimental effects on the ecosystem due to the production of harmful by-products, including heavy metals, inorganic substances, and persistent organic compounds, which can adversely impact both land-dwelling and marine ecology.

Objective: This review aims to provide a comprehensive overview of ionic liquid-based surfactants (ILBS), including their types, characteristics, advantages, and limitations, with a focus on their potential as "green surfactants" derived from or chemically synthesized from natural raw materials.

Method: The review synthesizes existing literature on ionic liquid-based surfactants, drawing from various sources including research articles, reviews, and academic publications. Relevant databases were searched using appropriate keywords related to ILBS, green surfactants, and their properties. Information on the types, characteristics, advantages, and limitations of ILBS was collected and analyzed to provide insights into their potential applications in the context of environmental sustainability and human health.

Results: Ionic liquid-based surfactants (ILBS) offer promising prospects as green alternatives to traditional surfactants derived from fossil fuel-based products. These surfactants possess unique properties such as low volatility, thermal stability, and tunable physicochemical characteristics, making them suitable for various applications in industries ranging from cosmetics to pharmaceuticals.

Conclusion: In conclusion, ionic liquid-based surfactants (ILBS) represent a promising avenue for addressing the environmental concerns associated with traditional cleaning products. By harnessing the unique properties of ILBS and exploring their potential applications in various industries, it may be possible to transition towards more sustainable and eco-friendly alternatives. However, concerted efforts are needed to overcome existing challenges and facilitate the widespread adoption of ILBS in commercial applications, thereby contributing to a cleaner and healthier environment for future generations.

1. Introduction

The advancement of industries in most financial marketplaces has accompanied with the advances accomplished through the continuous advances in science [1]. These inventions and technology utilise ecological reserves, such as hydrocarbon such as crude oil, fossil fuels, and similarly had an affirmative effect on current economy which ease to humans in our day to day life [2]. However, we can’t neglect harm causing to eco system by detrimental by-products, such as heavy metals and inorganic-organic compounds which combines or remained in land, waterways, and seas, are injurious to land-dwelling and aquatic ecology [3,4]. In the "The Paris UN Climate Conference 2015”, researcher came to conclusion related to a new form of development which is vigorous, sheltered and usable for all to meet the climate change challenge [12]. Therefore, scientists from the academic circles and the industrial circles should pay significant thought towards the negative effects of chemicals and chemical developments on the environment also alternative for the same.

Green Chemistry Principles

In the 1990s, *Paul Anastas* and *John Warner,* postulated the 12 principles of Green Chemistry, which are applicable till today. These principles rely on reuse, reducing use of toxic solvents in chemical processes and analyses and recycle, that mean designing of reaction with zero or degradable by-product. These principles are recommended globally from initiating product planning

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to its synthesis, processing, analysis and its application as end product. [6].

The green chemistry influences each and every industry. Green Chemistry encourages pathways that preserve energy, prevent the formation of waste, and utilize catalysis routes. It also encourages the reduction or replacement of organic solvents with water or solvent less processes [12]. To accomplish these goals, industry has implemented techniques such as sourcing new raw materials from biomass, use of alternative reaction conditions, and non-toxic reagents [7,8,9].

Green chemistry is not a separate science, but a viable approach to existing methods.

- **Prevention**
- **Atom Economy**
- **Less Hazardous Chemical Syntheses**
- **Designing Safer Chemicals**
- **Safer Solvents and Auxiliaries**
- **Design for Energy Efficient**
- **Use of Renewable Feedstocks**
- **Reduce Derivatives**
- **Catalysis**
- **Design for degradation**
- **Real-time analysis for pollution prevention**
- **Safer chemistry for accident prevention**

Figure 1. The 12 principles of Green Chemistry [6, 7]

3. Surfactant and their types:

The word surfactant is a combination of the terms *surf*ace *act*ive age*nts*, having binary characteristics of hydrophilicity and hydrophobicity. The term Surfactant itself suggests the surface-active nature of these classes of composites and their tendency to adsorb at interfaces. A Surfactant molecule consists of two parts of opposite affinity. The polar portion exhibits a strong affinity towards polar solvents, and it's frequently called hydrophilic part/ head. The apolar part is called hydrophobic or lipophile having affinity concerning to oil molecules that forms the tail part. Surfactants act by reducing the surface tension in between the two surfaces. [13] The effectiveness of a surfactant is determined by its capability to reduce surface tension, which is the mechanical energy needed to produce a unit new area of a liquid face. [12] Surfactants increase the aqueous solubility of hydrophobic compounds by decreasing the surface/ interfacial tension of air-water and oil-water interfaces. [14]

Activities of Surfactants:

- Solubilising agents act at low concentration and at or near to the critical micellar concentration, CMC.
- Foaming/ Defoaming agents act by absorbing at gas/liquid interfaces.
- Wetting or spreading agents act by reducing solid- liquid surface tension, particle once wetted allows liquid to spread more easily.
- Emulsifying agent aids in forming emulsion of two immiscible liquids.
- Dispersing agent helps in creating dispersion, more useful in paints and agrochemicals.
- Detergents helps in removal of dust or oily matter and thus cleaning. Detergency is a combination wetting, dispersion and emulsification of dust so ease ii eliminating the dust.
-

3.1 Classification of surfactants:

3.1.1 Types of surfactants depending on their charge at head space: [16]

As shown in Table 1, below are the type of surfactant based on their head charges.

Table 1. Types of surfactants depending on their charge at head space

Sr. No.	Type of Surfactant	Type of charge	Significance	Examples
1	Nonionic	No charge	45% of total industrial production; Harsh rarely used in cosmetics, used as wetting agents in coating industry	Ethoxylated aliphatic alcohols, Span
2	Cationic	Positive charge	Extremely harsh, commonly used in beauty products	Quaternary ammonium salt

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3	Anionic	Negative charge	50% of overall industrial production, lathers well thus used as in laundry detergents, dish washers	Soaps, Alkyl sulphates
4	Amphoteric/ Zwitterion	Both positive & negative charge	Expensive, specially used in cosmetics	Betaines, Amphoacetates

3.1.2 Types of surfactants depending on their origin: [10,13]

3.1.2.1 Synthetic (Chemical) Surfactants:

These are prepared using non-renewable feedstock such as petrochemicals, oils, gas, fossil fuels. [16] And include reactions especially cracking of non-renewable feedstock, that yields unsaturated, short-chain hydrocarbons, as well as enables locating of hydrophobic structures of surfactant molecules through polymerization of these alkenes, such as ethylene or propylene, giving rise to surfactants with C9 to C18 carbon chains. These are again additionally processed or reacted to form a variety of surfactant molecules (including those of alkylation, ethoxylation, or sulfonation). [14] In order to achieve task specific physical and performance properties the molecular structure may be altered during reaction process, itself. [16] The simple reactions from which synthetic origin surfactant can be obtained which are as shown in Table 2 below. [14, 15,17]

Table 2. Reactions by which various surfactants obtained

Sr. No	Reaction name	Reactants	Product
A	Sulfonation	Alkylbenzene and SO3 trioxide	Alkylbenzene sulfonates
B	Esterification	Aliphatic-aromatic alcohols and SO3	Long chain esters of a mineral acid (Sulfuric/ Phosphoric acid)
C	Esterification	Carboxylic acid) and fatty alcohol/ sugars	Esters of fatty acids
D	Ethoxylation	Ethylene oxide and a fatty alcohol	Ethoxylated fatty alcohols
E	Alkylation	Amine and a haloalkane	Long chain or substituted Alkylamine

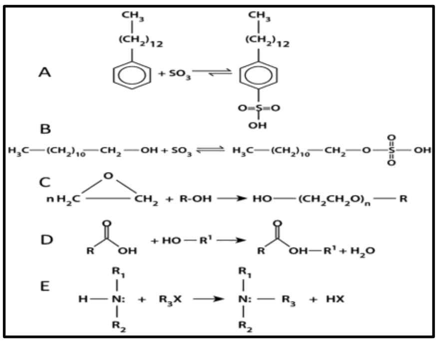

Figure 2. Reaction between DDB and SO3 to form anionic surfactant DDBSA (A). Reaction between DDC and SO3 forming the surfactant HDS (B). Ethoxylation between EO and alcohol (C). Esterification between a R-COOH and R-OH, forming ester and water (D). Reaction of a 2º amine with halide, forming 3º amine (E). (DDB: dodecyl benzene; DDBSA: dodecylbenzenesulfonic acid; HDS: hydrogen dodecyl sulfate; DDC: dodecanol: EO: ethylene oxide)

Boundaries of Synthetic Surfactant:

Surfactants being a multifarious molecule that are applicable mainly to decrease/ balance the facial tension in between the two different phases. These properties made them available to a wide range of industrial applications ranging from oil-recovery, agriculture, cosmeceuticals, pharma, textiles and food industries [19]. Most of the synthetic surfactants presently are budgetary since they are derived or synthesized at much low cost, however possesses noxious and obstinate components [18]. Today's main distress is the hazardous effects on the environment and ecological system. These surfactants have slow degradation, as a conclusion, they could accumulate or make derivatives that are detrimental to the natural environment [20].

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Reduction in species variety, rise in plant and animal biomass, rise in turbidity, raise in the rate of sedimentation, and decrease in the lifespan of the lakes are detrimental effects due to eutrophication.[21] As synthetic surfactants are chemically derived, generated from petroleum and products. They are very slow or not biodegradable and release various chemical compounds which persist in the environment and cause environmental pollution, eutrophication. Soil eutrophication leads to the speedy and tremendous growth of algae and other plankton which consumes the O_2 dissolved in water, suffocating to aquatic plant and animal life, as a result many desired aquatic species are at danger or vanished. In early 1960s, Johnson P et.al signified those foams generated by alkylbenzene sulfonates (ABSs), anionics such as sodium dodecyl sulfate (SDS) which is majorly applied in washing detergents, domestic and special cleaning products cover over bodies of water, such as rivers and lakes that received wastewater from big towns, which led to an ecological disproportion since the thick layer of foam subdued photosynthesis and O_2 dissolution [23]. The authorities of developed countries passed environmentally friendly laws to limit the usage of Synthetic surfactant in around 1965. Though, these synthetic based surfactants are still a continued to be a concern of sewage treatment facilities, in addition to of potable resources like lakes and rivers, in developing countries [22]. Another example is fluorinated surfactants, a subgroup of polyfluoroalkyl substances (PFAS), which were introduced in the 1940s and are very effective surfactants. Because of their inert properties, they were originally considered safe and were widely used. Today, however, they are considered as persistent organic pollutants that need to be replaced with environmentally friendly alternatives [24]. As well, Petro-based surfactants will soon start facing problems of raw material shortages due to the rapid exhaustion and enervation of petroleum and fossil fuels soon. Hence industries and researchers worldwide have shifted their attention to biobased surfactants to tackle this issue [16].

Biosurfactants are eco-friendly, biodegradable, and hence are a better alternative to petroleum-based surfactants [13].

3.1.2.2 Bio- based (Green) surfactant:

Researchers always have an interest to search or develop a novel product which would be improved, more effective, as well as safe to the environment, and health of the living being. This include adding a new group of surfactants for the various functions and procedures. One such class comprises of bio-based surfactant which has develop more extensively in the current era. The number of research articles were included day to day relating to Bio based or green surfactants, which enlighten the application of renewable origin surfactants or green surfactants or also identified as biosurfactants.

According to USDA (United States Department of Agriculture) definition, the bio-based surfactants are prepared from renewable domestic agricultural resources (including plant, animal, marine materials) or from forestry ingredients or from whole or substantial part of biological products [26]. In short, all bio-based surfactants are produced nonetheless in part from renewable feedstock, bio based and raw materials [18]. Natural Sources gives bio-based surface-active agent (i.e., both the head and tail molecular group) [13]. Generally, bio-based surfactants are prepared by chemical routes but sugars, fats or amino acids prepared from renewable sources, whereas microbial surfactants are attained from living cells, such as bacteria and yeasts, without organic synthesis routes [25].

Nowadays, biosurfactants are noticing interest as a promising product in industries like cosmetics, petroleum, agriculture, detergents, medicine, and food due to their constructive properties. Biosurfactants are substantial natural biodegradable substances retained to replace the chemical surfactants on a global scale in order to make a better and obviously causing minimum harm to ecology [13].

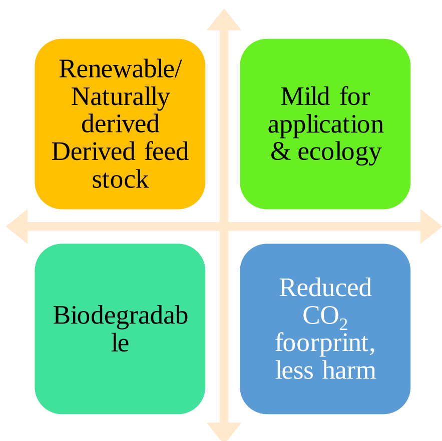

Figure 3: Benefits of Bio based surfactant

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Environmental regulation and governmental limitations related to the usage of poisonous detergents in products have also provided to the development and use of biosurfactants equally promising substitutes to synthetic surfactants [11]. Due to their functional similarity and low toxicity, the alternative of chemical surfactants with these natural materials has been investigated [8]. Certainly, biosurfactants or ‘‘green surfactants” are known as the forthcoming industrial surfactants, these mixtures meet most of the necessities for low eco-friendly impact industrial projects [19,20]. These surfactants are called as bio based or natural based surfactants, as they have obtained from natural sources e.g., marine, microbes and plants [27].

Microbial Surfactants

Microbial biosurfactants are the class of surfactants prepared from living cell [28, 29]. In fact, these are the secondary metabolites created by different microbs, such as yeast, bacteria and fungus [30]. Thus, are also called as 2nd generation biosurfactants which are obtained from microbial origins. Microbial genera including *Pseudomonas aeruginosa, Bacillus subtilis, Candida albicans, and Acinetobacter calcoaceticus* as main species researched considerably for their production. [37,77] Commonly microbial surfactants that are produced, are extracellular e.g., lipopeptides and glycolipids [31, 32]. On the other hand, some microorganisms can make microbial biosurfactants associated to the plasmatic membrane, and these are known as cell-bound microbial biosurfactants e.g., glycolipids and glycolipopeptides [33,34,35].

Microbial biosurfactants can be classified as [78, 79]

i) <u>Low molecular weight</u> (LMW), that includes glycolipids and lipopeptides,

ii) <u>High molecular weight</u> (HMW) which are generally polymeric compounds, e.g, polysaccharides, proteins and/or combination of lipoproteins or lipopolysaccharides [78]

Production of Microbial biosurfactant depends basically on the microbial strain, source of carbon and nitrogen i.e., substrate used, pH, temperature, and concentration of oxygen and metal ions. Microbial surfactants are linked with different stages of microbial growth. The type of biosurfactant generated is manipulated by the substrate and the pathway employed by the microorganisms for generation of surfactant [19]. Microbial surfactants are composed of amphiphilic surface-active substances and based on their molecular weight, they are subdivided into low or high molecular weight biosurfactants [38]. Microbial surfactants have different fundamental characteristics, such as the decrease in inter facial surface tension, emulsion formation, surface adsorption, micelle formation, etc. [24]

Table 3 Comparative study of Microbial and synthetic surfactant

Sr. No.	Microbial surfactant	Synthetic Surfactant
1	Biodegradable	Slow or not biodegradable
2	Very low Toxicity	Highly Toxic, Hazardous gas emission, Ozone layer depletion
3	Environment friendly, use renewable feed stock	Contribute to eutrophication, global warming
4	Costlier to manufacture	Cheap and money making
5	Technologies are yet under development to manufacture in high amount to fulfil market requirements	These can be produced at large scale to fulfil market requisite

Amino Acid/Peptide Based Surfactants

Amino acid surfactants (AAS) are biocompatible and biodegradable surfactants obtained by condensation of natural amino acids with fatty acids (or their derivatives) of oleochemical source [82- 84]. Hydrolysis of triglycerides from animal fat or vegetable oils gives a wide variety of saturated and unsaturated fatty acids with straight hydrocarbon chains and an even number of carbon atoms due to their biosynthetic route [85, 86]. AAS are a promising class of biocompatible and biodegradable surfactants for applications in pharma and biotechnological sector, owing to their biocompatibility and ecological compatibility [80]. The use of non-edible waste cooking oils is also a viable alternative, and further contributes to reduce the environmental burden [87]. The AAS market has been experiencing significant growth in recent years due to their eco-friendly nature and

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biodegradability. These surfactants are derived from natural sources such as coconut oil and plant proteins, assembling as a sustainable alternative to traditional surfactants. The demand for amino acid-based surfactants is expected to further increase in the coming years due to the rising awareness about environmental concerns and the shift towards green and natural products [90].

Additionally, AAS can be produced in large scale by green chemistry approaches, including enzyme-catalysed synthesis using immobilized lipases and proteases, although chemical processes still prevail due to high yields and low production costs [88, 89]. The trend toward green surfactants entirely produced from natural renewable sources by environmentally friendly technologies can change this scenario [80]. The presence of an amino acid as the polar headgroup characterizes AAS. The 20 standard amino acids used as the building blocks of proteins are the natural choice as raw materials for the production of AAS. These are amphoteric compounds and exist as zwitterions at physiological pH [83]. The hydrophobic chain can be introduced through acyl, ester, amide, or alkyl linkage. Gemini AAS are made of two amino acid headgroups and two hydrophobic chains per molecule joined by a spacer chain at or near headgroups. the Gemini AAS show better performance compared to their monomeric counterparts, such as lower CMC, higher efficiency in surface and interfacial tension reduction, and higher solubilization capacity [80, 81] The higher surfactant properties molecules by varying chemical structure, length, and number of fatty acid chains would be wide-ranging for nonpolar long-chain compounds (hydrophobic moiety) attached with polar amino acids/peptides (hydrophilic moiety) [39].

Therefore, saturated single-chain, double-chain, and gemini surfactants with different ionic characteristics have been discovered to be in all cases significantly biodegradable, low toxicity effects [40]. M.R. Infante et al., stated that for most of the properties gemini surfactants are better to the subsequent conventional monomeric surfactants. They are even more effective surface-active molecules than the single chain structures; approximately 3 times of magnitude for the equilibrium surface tension and about 20 times for the tension equilibration and foam stability [42, 43]. As per the global market size of amino acid-based surfactants was estimated at USD 528.58 million in 2021 and is anticipated to reach USD 1163.05 million by 2028, with a CAGR of 11.92% during the prediction period [44].

Table 4. General class of Amino acid-based surfactant and their application

Sr No.	Amino acid group	Application
1	Glutamic Acid-Based Surfactant	Excellent Cleansing Properties and Mildness on The Skin
2	Glycine Based Surfactant	Offer Gentle Cleansing Properties and Are Often Used in Personal Care
3	Sarcosine-Based Surfactants	Foaming And Emulsifying Abilities Used in Cosmetics for Hair Application.
4	Alanine-Based Surfactants	Excellent Foaming and Conditioning Properties, Used in Shampoos

Glycerol-Based Surfactants

Glycerides or acylglycerols are the esters prepared from glycerol and fatty acids. A series of novel glycerol-based non-ionic surfactants were synthesized from the trans esterification of various long chain fatty acid methyl ester with glycerol ester of dibasic acid (succinic acid, and adipic acid) [91]. Glycerol has 3 hydroxyl (-OH) functional groups, all of which can be esterified with one, two, or three fatty acids to form specific mono, di, and tri esters [45]. Triglycerides are the part of Fats and vegetable oils which can be split down into mono and di (also known as partial glycerides) due to the action of natural enzymes. Direct esterification method can be used to get Glycerol-based surfactants from glycerol and fatty acids. Transesterification can be used to get glycerol-based surfactant from reaction of glycerol and natural fats/oils or fatty acid methyl esters. High temperature and inorganic catalysts are used to get mono- and diglycerides by glycerolysis of fats and oils [1,46]. Chemical synthesis on a large scale is based on the glycerolysis of fats and oils at high temperatures using inorganic catalysts. The global polyglycerol esters market was valued at USD 9.8 billion in 2021 and is expected to reach USD 15.24 billion by 2029, with a CAGR of 5.60% during the projected period of 2022–2029 [46].

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4 Ionic Liquid Based Surfactants (ILBS):

Ionic liquids can be defined as the organic salts with low melting points, that are liquids in nature at or near room temperature. The head group and side chains, consisting of the cation and the accompanying anion are the major parts of an IL structure. They are also known as "ionic melts," "ionic fluids," "fused salts," "liquid salts," "ionic glasses," "solvents of the future" "room temperature molten salt," "low-temperature molten salt," "ambient temperature molten salt," or "designer solvents." in the literature [47, 48]. Ethyl ammonium nitrate $[EtNH_3][NO_3]$ (M.P. 12 °C) was the first IL, reported in 1914 by Paul Walden.[49]

Advantages of ILs:

- They are the green replacements for organic solvents for chemical reactions, extractions and biotransformation's.
- They are thermostable and have negligible vapour pressure and, thus useful as in a variety of fields such as extraction processes organic synthesis, nanoparticle synthesis, [50].
- By changing the cation and the anion substitution their solvency property can be altered and useful in chemical synthesis reactions.
- They are useful in various bio-catalytic processes, drug delivery, and pharmaceutical industries [50], [51].

Table 5: Comparison of Water as universal solvent Vs ionic liquid as solvent [51]

Plain Water		Pure ionic liquid	
Drawbacks	**Advantage**	**Advantage**	**Drawbacks**
Solubility	Cheaper, low viscosity	Tunability	Costly
Compatibility	Safety	Safety	High viscosity
Heat of evaporation	Environmentally benign	Reactivity	Availability
Corrosion	Hydrogen bond	Solvation Property	Unknown data

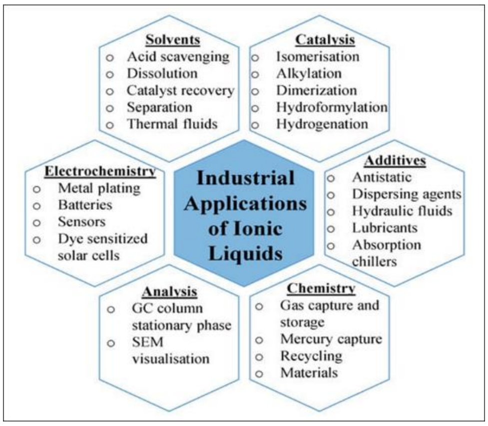

Figure 4: Applications of IL respectively Redrawn from [59]

Disadvantage of ILs - They are comparatively costly and also study yet to explore in terms of biodegradability, biocompatibility [53]

Ionic Liquid Based Surfactant (ILBS)

Currently surface-active ionic liquids in water give rise to distinct chemistry of their own compared to traditional moieties due to an emerging stress on sustainable technologies, ionic liquids have proved as task specific and environmentally friendly solution for multiple conventional industrial application., and thus their use is rapidly growing [57]. The amphiphilic class of ILs, are identified as Surface Active Ionic Liquid (SAIL) or Ionic Liquid Based Surfactant (ILBS). '*Amphiphilic ILs, with a hydrophilic head group and hydrophobic tail in their molecular structure are known as SAIL/ ILBS* [64], and hence form micellar aggregates in water. Like conventional surfactants, adsorption of ILBSs at the interface gives drop in Interfacial tension (IFT). [56] Additionally, properties such foaming and emulsifying activity [52, 56].

There are 5 major classes of cationic ILBSs [58] e.g. ammonium, pyridinium, imidazolium, phosphonium and sulfonium. Whereas variety of commonly used anions such as halides (chloride, bromide, and iodide), sulfate, sulfonate, phosphate, bis (trifluoromethanesulfonamide), tetrafluoroborate (BF_4), acetate, dicyanamide etc. The physico-chemical property such as viscosity, conductivity and melting point can be altered by modifying anionic moiety.

Advantages of ILBS: [56,58,60]

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- ILBS have low critical micelle concentration (CMC) and high solvency property,
- They have superior wetting and foaming properties,
- They are recyclable and give high performance under harsh conditions
- also give applications in the biological area such as Drug delivery, enzyme catalysis, biomolecule extraction, bio compound separation.
- They can also act as a *task-specific* ILBS by altering their cation and/ or anion structure. In this regard, many investigators have synthesized a variety of types and are being studied.

However, all ILBS are not always nontoxic or eco-friendly. There are some incidents, that have been reported e.g., unstable micellisation due to high concentration of the surfactant. ILBS pints the halogen-content of anions like $[AlCl4]^-$, $[PF6]^-$, $[BF4]^-$, etc. that may cross the permissible limit and results in hazards. [60] Even degradation of ILBS may lead to halide ions such as Cl^- and F^- halides. So, it is necessary to keep halide concentration within limit.

Synthesis of ILBS

Preparation of ILBS consists of 2 steps as below. [61, 62]

a) 4^o quaternization of phosphines or amines, typically carried out by the S_N2 mechanism. It is employed by use of haloalkanes, or alkyl sulphates and mostly by the Menshutkin reaction. The amine (or phosphine) is combined with the desired haloalkane, followed by stirring and heating. Menshutkin reaction involves use of refluxing of appropriate molecular solvent, e.g., acetonitrile. As it is SN2 reaction, it depends on the type of halide and alkyl group chain length effects the yield. For example, for haloalkanes, should have the expected order of RI > RBr > RCl (R = n-alkyl group); with an increase in the chain length of R decreases the reaction rate [55, 63].

b) Metathesis/ anion exchange: It is accomplished wherever necessary, to produce the desired product.

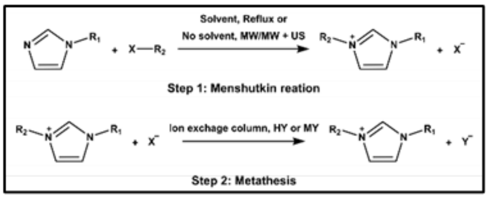

Figure 5 Schematic representation of the synthesis of ILs and ILBS. MW: Microwave and US: ultrasound irradiation [63]

Microwave [64] or a combination of microwave and ultrasound irradiation [65] can be used to prepare ILBS instead of solvent application for synthesis. The obtained products are classified as 1st generation ILs and ILBSs.

The result of a metathesis reaction is that 2nd generation ILs and ILBSs are obtained from alteration of their 1st generation counterparts. 2nd generation ILs and ILBSs has bulkier anions, e.g. $C_6H_5CO_2^-$ and $(CF_3SO_2)_2N^-$ BF_4^- , PF_6^- [65]. Single-chain ILBSs can be covalently coupled to form dimers which are gemini surfactants, (GILBSs), trimers, and polymeric ILBSs. This structure flexibility can be employed to acquire different structures [67].

Structure activity relationship of ILBS

The increase in the length of alkyl chain from C2 to C16 leads to eventual transformations from isotropic solution to worm-like micelles, as well as a hexagonal liquid crystal/ hydrogel to surfactant precipitation. Furthermore, these surfactants form thermodynamically stable microemulsions, such as in polymerization [66]. Enhancement in the ester functionality leads to biodegradation of ILs; besides, substitution of a methyl group to the 2-position of the imidazolium cation and use of alkyl sulfate as a counter-ion also advances the biodegradability [66]. As ILBS are being liquid and solid in state, the prominent features such as suitable ion conductivity, low-level vapor pressure, solvation capability, chemical and thermal stability, non-flammability, high polarity, are found over a wide range of temperature [61,63,69]. Furthermore, ILBSs have been proposed with required properties regarding resistance, environmental compatibility, and recycling under harsh conditions such as high salinity. It is feasible to design ILBS molecules are design for task-specifc works by changing their cation and/ or anion structure. Many researchers have created a variety of cationic, gemini, and zwitterionic ILBSs with enhanced surface activity [57].

The demand for reducing interfacial tension (IFT) in various processes has led investigators to use balanced and resistant surfactants with minimal environmental influence. ILBSs have gained considerable attention due to their excellent amphiphilic nature and outstanding properties such as recyclability and high performance under harsh conditions [70]. Nevertheless, maximum IL surfactants are not environmentally friendly and gives

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unstable micelles, even while using a high strength of the surfactant. In this study, author has synthesized a series of halogen-free and biocompatible choline–fatty-acid-based ILBSs with different chain lengths and degrees of saturation, and then explored their micellar properties in aqueous media. Characterization of the prepared ILBSs was done by 1H and 13C NMR, FTIR spectroscopy, DSC, and CHNS analysis [60].

Physical Characteristics of ILBSs

ILs are made up of organic cations and inorganic or organic anions, having melting point of range well below 100 °C. and at room temperature they form stable liquid phase. The head group and side chains, consisting of the cation and the anion are the major parts of an IL structure.IL consists of typical yet simple cations like ammonium ion, phosphonium ion, sulfone ion, an/ or heterocyclic cations like pyridinium, piperidinium pyrrolidinium, and imidazolium, ions coupled with different inorganic or organic anions, ranging from simple inorganic ions to complex organic groups. Some typical IL anions are sulphate, sulfonate, dicyanamide phosphate, borate, tetrafuoroborate, tricyanomethide, bis(trifuoromethylsulfonyl) imide, benzenesulfnic, and halide [70].

Table 6 Comparison between ILBS and Conventional surfactants [71]

Properties	Ionic Liquid Based Surfactant	Conventional Surfactants
Interfacial Tension (IFT)	They are effective in Enhanced oil recovery application as can reduce IFT up to 10^{-2} mN/m	They can reduce IFT up to 10^{-4} - 10^{-3} mN/m , less effective in EOR applications.
Toxicity	Many of the ILBS are less noxious and environmentally safe for different applications	These are considerabl yhazardous in nature.
Stability	They are stable for wide temperature range and can be stowed without decomposition	They give uncertain shelf life and surfactant at high temperature
Viscosity	The viscosity of ILBS can be manipulated by deviations in branching and probable high viscosity canbe achieved.	They are unable to attain high viscosity in aqueous solution

Merits of ILBS

ILBS have many advantages over conventional surfactants as recognized below [71,72]

1. ILBS are easily accessible for various applications since they have melting point well below 100 °C.
2. ILBS are tunable molecules with the change of numbers of cations and anions combination as per the end use application. [28, 40].
3.Some ILBS based on cations or anions have a relatively higher viscosity that surfactant solution, which is favourable in a change of mobility ratio [75].
4. Unexpected thermal and chemical stability [73,74].
5. ILBS are cost-effective and commercially available [58].
6 Owing to robust cohesive forces ILBS have, they can form stable micelles without the need of additional cosurfactants [76,54].
7. They are usually non-flammable and have a wide range of solubility and miscibility [75]

Demerits of ILBS

Again, some representative serious issues are shown by ILBS while they consist of halogen-containing anions like [CF3SO3]$^-$ [(CF3SO2)2N]$^-$, [AlCl4] $^-$, [PF6]$^-$, [BF4]$^-$, which cross the limit of greenness that means harmful to ecology. Hydrogen Chloride and Hydrogen Fluoride produced during degradation of ionic liquids that consist of halides viz Cl^- and F^-. So, we should take care of the properties of these ILBS during synthesis. [77]. Another limitation is impurities of ionic liquids. Impurities of ILBS can render their effectiveness.

Conclusion:

Overall, this review explains about role of surfactants and their application.; differentiation between conventional synthetic based and green surfactants. Also, enlights harms that has caused due to synthetic surfactants though they are comparatively cheap they are causing a huge drawback to ecosystem which would suffer over a year. Researchers are working on to the increasing manufacturing capacity of the green surfactant.

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