Amphiphilic Ionic Liquid Assisted Detoxification of Pollutants: A Critical Review

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Abstract: *The escalating contamination of water bodies by persistent organic and inorganic pollutants is one of the most urgent environmental challenges of the 21st century. Conventional treatment methods—physical, chemical, and biological—are often inefficient, energy-intensive, or generate secondary pollution. Electrochemical technologies offer rapid kinetics, mild operation, and minimal chemical input, yet they are hampered by electrode fouling, high cost, and poor solubility of hydrophobic pollutants. This critical review presents a comprehensive evaluation of an emerging paradigm: the use of amphiphilic ionic liquids, specifically surface-active ionic liquids (SAILs), as both electrolyte and micellar medium for the electrochemical sensing and detoxification of priority pollutants, with a focus on halocarbons. SAILs self-assemble into nanomicelles that solubilise hydrophobic contaminants, eliminate the need for supporting electrolytes, and provide a high-surface-area interface that mimics the catalytic activity of metal nanoparticles—without their toxicity. We critically analyse the synthesis, physicochemical characterisation, and electrochemical behaviour of imidazolium-based SAILs, dissect the mechanisms of dissociative electron transfer in micellar media, and compare performance with conventional electrodes and nanoparticle systems. Key research gaps are identified, including long-term stability, scale-up challenges, and the need for comprehensive ecotoxicity assessments. The review concludes that SAIL-assisted electrodetoxification holds exceptional promise as a green, economical, and scalable technology, provided that future work focuses on rational molecular design, continuous-flow reactor engineering, and life-cycle environmental impact.*

Keywords: Amphiphilic Ionic Liquids, Surface-Active Ionic Liquids, Electrochemical Detoxification, Halocarbons, Micellar Catalysis, Green Chemistry, Wastewater Treatment.

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Introduction

The conservation of environmental resources has progressively emerged as a matter of paramount social concern, necessitating rigorous sustainable development strategies to prevent the depletion and degradation of natural resources. Governments worldwide have enacted increasingly stringent legislation governing safe effluent discharge, reflecting growing awareness of the ecological and public health consequences of unchecked industrial pollution. Wastewater treatment currently encompasses a diverse array of methodologies designed to detoxify waters containing organic and inorganic pollutants, employing traditional techniques grounded in physical, chemical, and biological principles, as well as advanced oxidation processes [1–3].

Biological treatments remain the most prevalent methods for wastewater remediation; however, they are time-consuming, require substantial operational areas, and demonstrate incomplete efficacy against many environmental toxic pollutants. While such techniques represent the state of the art in municipal water treatment, they are inadequate for treating industrial effluents containing high concentrations of organic pollutants and landfill leachates [1]. Traditional physicochemical processes are comparatively ineffective, expensive, and potential sources of secondary pollution. Advanced oxidative processes—ozonation, wet oxidation, heterogeneous photocatalysis, and the Fenton process—demand substantial energy consumption and expensive reagents [2,3].

These limitations underscore the critical need to develop highly sensitive, reliable, user-friendly, and economical tools for the relentless sensing, detection, and detoxification of pollutants across diverse environmental media. In this context, electrochemical technologies have emerged as particularly promising, especially for the treatment of wastewater containing toxic pollutants. The applications of electrochemical technologies to combat environmental pollution have been extensively documented in numerous authoritative reviews [3–9]. The electrochemical technologies utilised for wastewater detoxification primarily include electroflotation, electrocoagulation, electrodialysis, electrochemical oxidation, electroreduction, and mediated electrochemical reduction/oxidation [3].

Electrochemical detoxification offers distinguished features including rapid reaction rates, low apparatus costs, mild reaction conditions, and green processing technology that requires no extra chemical additives [10]. Moreover, it enables selective reduction of pollutants like halocarbons to completely halogen-free chemicals [11–14]. Despite these advantages, electrochemical technologies remain constrained by certain limitations, including the short lifetime and high cost of some electrode materials, as well as diminished current efficiency under specific conditions [15,16]. Furthermore, the influence of pollutant nature and concentration, pH, effluent conductivity, electrode arrangement, and the occurrence of undesired reactions on process performance has not been fully evaluated across all reported studies [3].

The emergence of ionic liquids (ILs) as novel solvents and functional materials has opened new opportunities in environmental protection. ILs possess many fascinating properties—negligible

vapour pressure, remarkable thermal stability, exceptional solvating capabilities, and tunable physicochemical characteristics—that distinguish them from conventional volatile organic solvents. The tunability of ILs enables precise adjustments in viscosity, polarity, and hydrophobicity, offering a versatile and task-specific resource for contaminant capture [17–19].

Among the various classes of ionic liquids, surface-active ionic liquids (SAILs) have garnered particular attention as environmentally benign alternatives to conventional surfactants. The combination of water and SAILs provides a unique reaction medium, facilitating aggregation and micellisation that enables chemical reactions in bulk water. SAILs offer customisable and readily functionalisable chemical structures, with imidazolium-based SAILs presaged as promising additives for desired alterations in the redox characteristics of diverse analytes. These potentialities, if intelligently employed, are expected to establish SAILs as innovative and task-specific alternatives to conventional surfactants and organic solvents in electrochemical investigations including electrocatalysis and electroanalysis [20,21]. To the best of our knowledge, there is not a single report published so far about the use of imidazolium-based SAILs either as additives or as solvents for electrosensing applications except one recent study for biosensing applications [22]. SAILs have been emerging as novel amphiphiles due to their unique physicochemical properties and efficient surface activity in comparison to conventional surfactants [23]. Further, such systems act as electrolytes and their aqueous solution could be used as media for electrochemical sensing and subsequent detoxification of organic pollutants without the use of any supporting electrolytes.

This critical review provides a systematic evaluation of SAIL-assisted electrochemical detoxification, covering synthesis, characterization, mechanistic insights, comparative performance, and future directions.

1. Surface-Active Ionic Liquids: Synthesis, Characterization, and Fundamental Properties

1.1. Structural Architecture and Design Principles

Surface-active ionic liquids integrate the characteristic properties of ionic liquids—negligible vapour pressure, high thermal stability, and tunable physicochemical properties—with the self-assembly and interfacial activity of conventional surfactants. The molecular architecture of SAILs typically comprises a bulky organic cation, frequently imidazolium, pyridinium, or pyrrolidinium derivatives, paired with an appropriate anion. The amphiphilic character is imparted through the incorporation of long alkyl chains into the cation structure, creating a distinct hydrophilic head group and hydrophobic tail region that drives self-assembly in aqueous media [23].

The design of SAILs with tailored properties requires careful consideration of several structural parameters. The choice of cation head group significantly influences the physicochemical properties, including critical micelle concentration (CMC), aggregation number, and micellar morphology. Imidazolium-based SAILs have emerged as particularly promising due to their established synthesis protocols, favourable electrochemical properties, and demonstrated biocompatibility [24]. The anion selection represents another critical design parameter that modulates SAIL properties. While halide anions (chloride and bromide) are commonly

employed, recent efforts have focused on developing halogen-free SAILs to minimise potential environmental impacts [25].

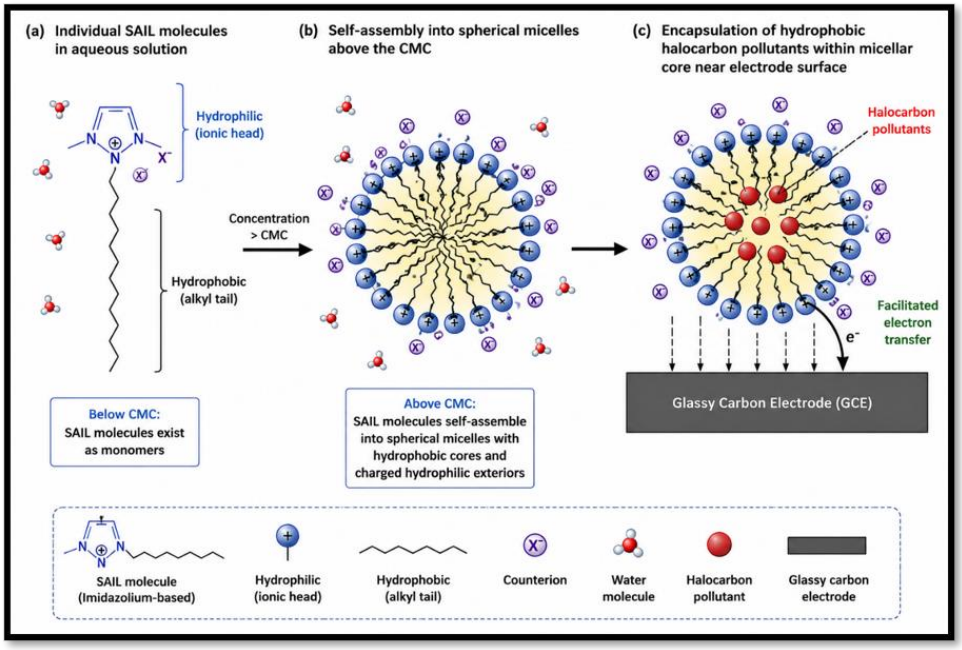

Figure 1: Schematic illustration of (a) individual SAIL molecules (imidazolium head with long alkyl tail) in aqueous solution, (b) self-assembly into spherical micelles above the CMC with hydrophobic cores and charged hydrophilic exteriors, and (c) encapsulation of hydrophobic halocarbon pollutants (red spheres) within the micellar core, with the micelle positioned near a glassy carbon electrode surface to facilitate electron transfer.

1.2. Synthesis Methodologies

The synthesis of SAILs generally proceeds through well-established routes involving quaternisation of the nitrogen-containing heterocycle with appropriate alkyl halides, followed by anion metathesis when necessary. The quaternisation reaction typically employs alkyl halides bearing long-chain alkyl groups (C8-C18) to impart the desired amphiphilic character. Reaction conditions—temperature, solvent, reaction time, and stoichiometry—must be carefully optimised to achieve high yields and purity [23].

For imidazolium-based SAILs, the synthesis involves the reaction of 1-methylimidazole with 1-bromoalkane or 1-chloroalkane under reflux in an appropriate solvent such as acetonitrile or ethyl acetate. The resulting 1-alkyl-3-methylimidazolium halide can be further subjected to anion exchange to introduce alternative anions with desired properties. Purification of SAILs presents particular challenges due to their amphiphilic nature; common methods include repeated washing with organic solvents, recrystallisation, column chromatography, and dialysis. Purity is typically verified through NMR spectroscopy, mass spectrometry, and elemental analysis [23,25].

1.3. Physicochemical Characterization

The characterisation of SAILs encompasses a comprehensive suite of analytical techniques. Tensiometry is fundamental for determining surface activity, enabling calculation of CMC, surface excess concentration, and minimum area per molecule at the air-water interface. The CMC provides critical insight into self-assembly behaviour and is influenced by alkyl chain length, head group structure, and anion identity [23].

Conductometry offers complementary information about aggregation behaviour in aqueous solution. The characteristic break in the conductivity versus concentration plot at the CMC reflects the reduced mobility of ionic species upon micellisation. Recent studies have employed conductometry in conjunction with UV-visible spectroscopy and cyclic voltammetry to comprehensively characterise SAIL aggregation [26].

Nuclear magnetic resonance (NMR) spectroscopy, particularly ^1^H-NMR, provides detailed information about the molecular environment and aggregation state. Chemical shift changes upon micellisation reflect alterations in the local magnetic environment experienced by protons in different regions of the molecule. Diffusion-ordered NMR spectroscopy (DOSY) enables determination of diffusion coefficients, providing insight into micellar size and aggregation numbers [27].

Surface tension measurements, conducted using the Wilhelmy plate or pendant drop method, enable determination of CMC and provide information about the efficiency and effectiveness of surface adsorption. The surface tension reduction achieved at the CMC reflects the surface activity of the SAIL, which is typically superior to conventional surfactants due to the ionic nature of the head group [23].

Electrochemical characterisation of SAILs encompasses determination of electrochemical windows, ionic conductivity, and electron transfer kinetics at electrode interfaces. SAILs exhibit wide electrochemical windows exceeding 4 V, rendering them suitable for diverse electrochemical applications. The ionic conductivity of SAIL solutions is influenced by concentration, temperature, and the nature of both cation and anion [26].

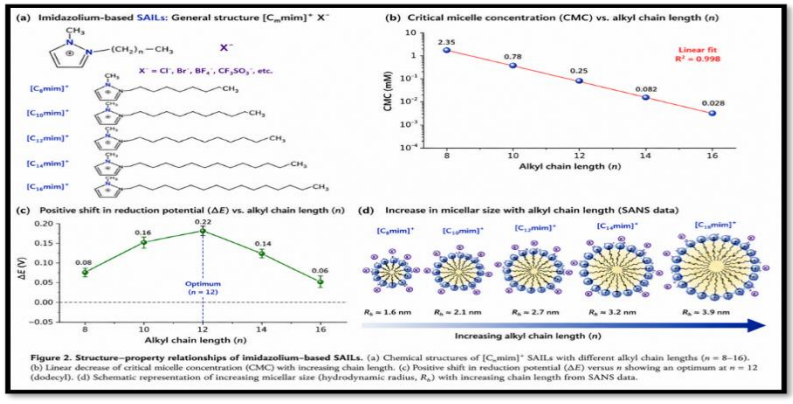

Figure 2. Structure–property relationships of imidazolium-based SAILs. (a) Chemical structures of $[C_n mim]^+$ SAILs with different alkyl chain lengths (n = 8–16). (b) Linear decrease of critical micelle concentration (CMC) with increasing chain length. (c) Positive shift in reduction potential (ΔE) versus n showing an optimum at n = 12 (dodecyl). (d) Schematic representation of increasing micellar size (hydrodynamic radius, R_h) with increasing chain length from SANS data.

Figure 2: Structure-property relationships of imidazolium-based SAILs: (a) chemical structures of $[C_n mim]^+$ with n = 8, 10, 12, 14, 16; (b) plot of CMC versus alkyl chain length

(n) showing a linear decrease with increasing n; (c) plot of the positive shift in reduction potential (ΔE) versus n, demonstrating an optimum at n = 12 (dodecyl); (d) schematic representation of increasing micellar size (from SANS data) with increasing chain length.

1.4. Micellisation Behaviour and Self-Assembly

The self-assembly of SAILs in aqueous solution is driven by the hydrophobic effect, wherein the entropically favourable release of water molecules from the solvation shell of the hydrophobic alkyl chains drives aggregation. The CMC is influenced by alkyl chain length, head group structure, counterion identity, temperature, and ionic strength [23].

The morphology of SAIL micelles depends on molecular geometry, concentration, and environmental conditions. Spherical micelles are typically formed at concentrations just above the CMC, with transitions to cylindrical or lamellar structures occurring at higher concentrations. The aggregation number—the average number of SAIL molecules per micelle—provides insight into micellar size and can be determined through light scattering, fluorescence spectroscopy, and small-angle neutron scattering [24].

The interface between the micellar core and the aqueous bulk phase represents a region of unique properties, with the charged head groups forming a structured interfacial layer. The electrostatic potential at the micellar surface influences the partitioning and reactivity of ionic species, including pollutant molecules and electroactive species. Recent studies have demonstrated that the micelle/water interface-localized SAIL units significantly enhance electrocatalytic performance toward electro-dehalogenation of halocarbons [28].

Electrochemical Detoxification of Pollutants: Principles and Challenges

Fundamentals of Electrochemical Pollutant Remediation

Electrochemical detoxification operates on the principle of applying an electrical potential to drive redox reactions that convert toxic pollutants into less harmful species. The process occurs at the electrode-electrolyte interface, where electron transfer between the electrode and pollutant molecules facilitates chemical transformation. The thermodynamic feasibility is governed by the applied potential relative to the reduction or oxidation potential of the target pollutant, while the kinetics are influenced by electrode material, mass transport, and the nature of the electrolyte [3].

The electrochemical degradation of organic pollutants can proceed through direct electron transfer at the electrode surface or through mediated processes involving electrogenerated reactive species. Direct electrochemical reduction involves the transfer of electrons from the cathode to the pollutant molecule, typically proceeding through a dissociative electron transfer mechanism for halogenated compounds. Direct electrochemical oxidation occurs at the anode, where electron withdrawal from the pollutant molecule initiates degradation [3–5].

Mediated electrochemical processes employ redox mediators—species that shuttle electrons between the electrode and the pollutant. Mediators can be homogeneous (dissolved in the electrolyte) or heterogeneous (immobilized on the electrode surface). The use of mediators can

enhance reaction selectivity, reduce overpotentials, and enable the degradation of pollutants that are otherwise electrochemically inactive at accessible potentials [6].

Halocarbons as Priority Environmental Pollutants

Among the diverse array of toxic environmental pollutants, halocarbons have received special attention due to their persistence, toxicity, and widespread distribution. Halocarbons find frequent applications in industrial processes, with subsequent disposal into wastewater streams. Halocarbons such as chloroform are also produced as disinfection by-products during the chlorination of wastewater. These compounds are highly stable and consequently resistant to oxidative remediation methods, emerging as among the most dangerous environmental pollutants [29–31].

The stability of halocarbons derives from the strength of the carbon-halogen bond, which increases with the electronegativity of the halogen. The carbon-chlorine bond, for example, exhibits bond dissociation energies ranging from approximately 330 to 400 kJ/mol depending on the molecular environment. The resistance of halocarbons to oxidative degradation stems from the electron-withdrawing nature of halogen substituents, which deactivate the molecule toward electrophilic attack [29].

The toxicity of halocarbons encompasses acute toxicity, carcinogenicity, and endocrine-disrupting effects. Chloroform, carbon tetrachloride, and other chlorinated solvents are classified as probable human carcinogens, with chronic exposure associated with liver and kidney damage. The environmental persistence of halocarbons results in bioaccumulation and biomagnification through food chains, posing risks to both ecosystem health and human populations [30].

Electrochemical Reduction of Halocarbons

Electrochemical reduction has been successfully employed for several decades, not only to convert halocarbons to less harmful compounds but also for organic electrosynthesis [31–34]. The electrochemical reduction of halocarbons proceeds through the cleavage of carbon-halogen bonds, yielding hydrocarbon products and halide ions. The overall reaction is:

$$R\text{-}X + 2e^- + H^+ \rightarrow R\text{-}H + X^-$$

The mechanism has been extensively investigated, revealing both stepwise and concerted dissociative electron transfer pathways. The stepwise mechanism involves initial electron transfer to form a radical anion intermediate, followed by cleavage of the carbon-halogen bond to yield a carbon-centered radical and halide ion. The concerted mechanism involves simultaneous electron transfer and bond cleavage, with no detectable intermediate [35].

The reduction potential required for halocarbon dehalogenation depends on the nature of the halogen, the molecular environment, and the electrode material. Carbon-halogen bond cleavage becomes progressively more difficult in the order C-I < C-Br < C-Cl < C-F. The reduction of polychlorinated compounds occurs through sequential dechlorination steps, with each successive chlorine removal becoming more energetically demanding [36–38].

Electrode Materials and Electrocatalytic Effects

The choice of electrode material exerts a profound influence on the efficiency and selectivity of halocarbon electroreduction. Different electrode materials exhibit varying catalytic activities, enabling reduction at less negative potentials. For example, a positive shift of 1.2 V in the reduction potential of halocarbons has been observed on silver electrodes compared to glassy carbon electrodes [38].

The electrocatalytic properties of electrode materials are attributed to several factors including the electronic structure of the metal, the adsorption energy of reactants and intermediates, and the surface morphology. Silver and copper electrodes have demonstrated excellent catalytic activity for halocarbon reduction. Silver nanoparticles have exhibited comparable or even superior electrocatalytic properties to bulk silver for halocarbon reduction [39–42].

The enhanced catalytic activity of nanostructured electrode materials is attributed to their increased surface area, high density of low-coordination surface sites, and unique electronic properties. However, nanoparticles are inherently unstable and require immobilisation on electrode surfaces using supporting materials such as Nafion. Furthermore, metal nanoparticles are toxic, limiting their application in household water treatment devices [43,44].

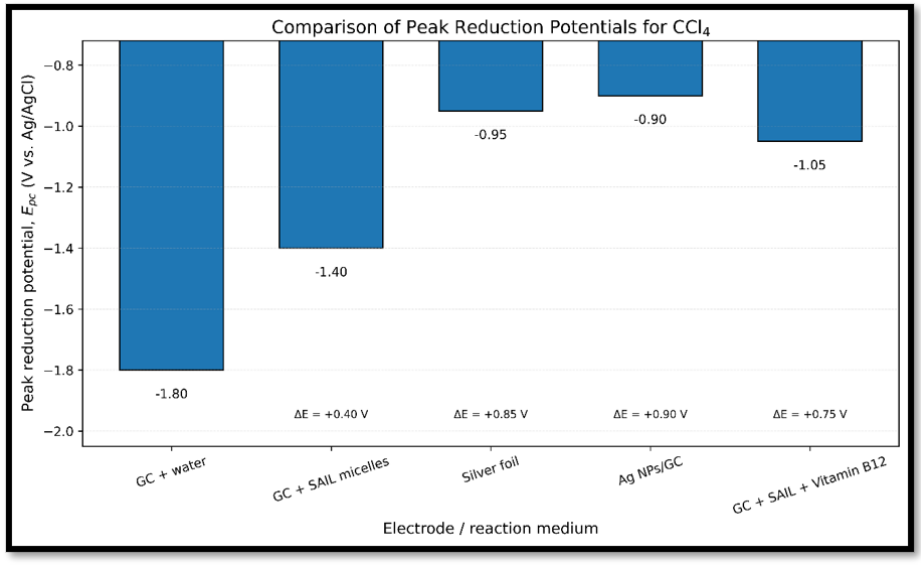

Figure 3: Comparison of peak reduction potentials (E_pc) for a model halocarbon (CCl_4) on different electrode materials: (a) glassy carbon (GC) in water (–1.8 V vs. Ag/AgCl), (b) GC in SAIL micellar solution (–1.4 V), (c) silver foil (–0.95 V), (d) silver nanoparticles on GC (–0.90 V), and (e) GC in SAIL + vitamin B_{12} mediator (–1.05 V). The data demonstrate a significant positive shift (up to 0.9 V) for SAIL-based systems, approaching the performance of noble metal nanoparticles.

Amphiphilic Ionic Liquid-Assisted Electrochemical Detoxification

Rationale and Conceptual Framework

The limitations of conventional electrode materials and the environmental concerns associated with metal nanoparticles have motivated the search for alternative approaches to enhance electrochemical detoxification efficiency. The proposal that aqueous systems containing nanomicelles could behave similarly to metal nanoparticles—owing to their enhanced surface area—represents a paradigm shift in electrochemical detoxification strategy [28].

Surface-active ionic liquids present a particularly promising platform for this approach. SAILs are environmentally benign, potentially serving as substitutes for toxic metal nanoparticles, organic solvents, and conventional surfactants. Moreover, SAIL solutions can function as electrolytes, eliminating the need for supporting electrolytes and simplifying the electrochemical system. The aqueous micellar solutions of SAILs provide a unique reaction medium that combines the solvent properties of water with the solubilisation capacity of micelles [23,28].

The conceptual framework for SAIL-assisted electrochemical detoxification rests on several key principles. First, the micellar aggregates provide a high-surface-area interface that can mimic the catalytic properties of nanoparticles. Second, the hydrophobic micellar cores can solubilise hydrophobic pollutants, overcoming the poor solubility that often limits electrochemical treatment in aqueous media. Third, the charged micellar surface can influence the partitioning and reactivity of ionic species, potentially enhancing electron transfer kinetics. Fourth, the SAILs themselves can participate in the electron transfer process, functioning as redox mediators [28].

Aqueous Micellar Solutions of SAILs as Electrochemical Media

The electrochemical behaviour of halocarbons in aqueous micellar solutions of imidazolium-based SAILs has been investigated, demonstrating that these systems facilitate electroreduction. The electrochemical reduction of carbon tetrachloride (CCl_4) in aqueous micellar solutions of dodecylmethylimidazolium chloride ([DDMIM]Cl) has been shown to follow a sticky dissociative pathway. The micellar solutions of [DDMIM]Cl facilitate the electroreduction of CCl_4, presenting a promising approach for eco-green electrodetoxification [28].

The mechanism of halocarbon electroreduction in SAIL micellar media involves several key steps. The hydrophobic halocarbon molecules partition into the micellar core, where they are effectively concentrated and protected from the aqueous environment. The micelle-water interface provides a unique environment where electron transfer can occur, with the charged imidazolium head groups potentially stabilising transition states and intermediates. The reduction process ultimately yields dehalogenated products and halide ions, with the products partitioning out of the micellar core into the aqueous phase [28].

Recent studies have demonstrated that redox-couple mediation represents a promising strategy to enhance the electrocatalytic performance of SAIL interfaces. The negatively charged redox

mediator interacts with the imidazolium head groups localised at the micelle-water interface, significantly enhancing the electrocatalytic performance of aqueous micellar solutions of [DDMIM]Cl toward electro-dehalogenation of halocarbons. This mediation approach offers a route to further improve the efficiency and selectivity of SAIL-assisted electrochemical detoxification [28].

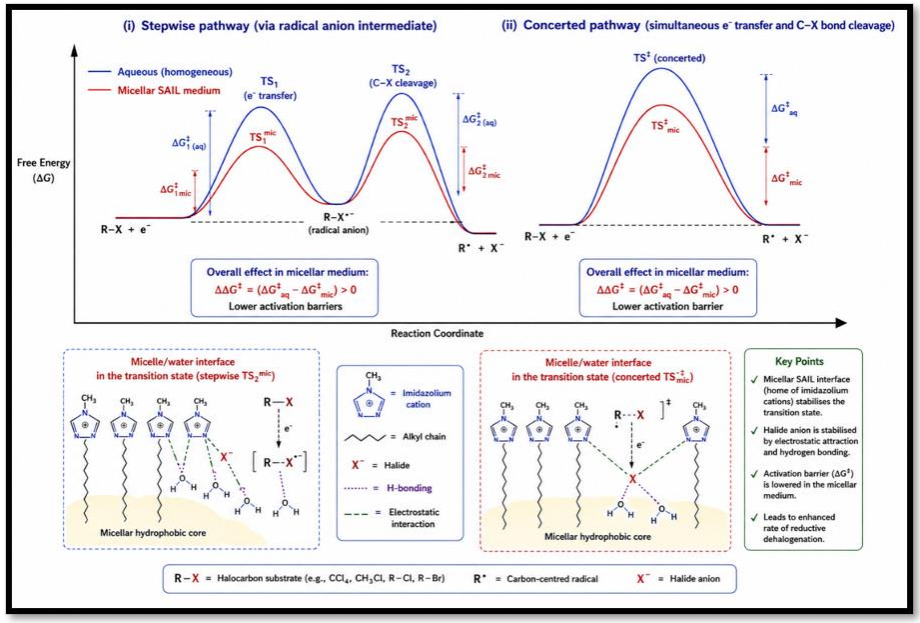

Figure 4: Energy diagram (reaction coordinate vs. free energy) for the reductive dehalogenation of a halocarbon (R-X) in aqueous micellar media. Two pathways are shown: (i) the stepwise pathway involving a radical anion intermediate (R-X•⁻), and (ii) the concerted pathway with simultaneous electron transfer and bond cleavage. In the micellar medium (red curve), the charged imidazolium interface stabilises the transition state (indicated by the stabilisation energy ΔG‡_{mic}), leading to a lower activation barrier compared to the homogeneous aqueous medium (blue curve). The insets depict the molecular arrangement at the micelle/water interface, with the imidazolium cation stabilising the leaving halide through electrostatic and hydrogen-bonding interactions.

Electrochemical Sensing and Detection in SAIL Media

The applications of SAIL-based systems extend beyond detoxification to encompass the sensing and detection of environmental pollutants. Ionic liquid-based materials have been employed for electrochemical sensor applications in environmental samples, with recent reviews overviewing the latest applications of ILs-based materials modified electrochemical sensors for determining environmental contaminants such as drug residues and pesticides [45]. The use of SAILs as both solvents and electrolytes for electrochemical sensing offers several advantages. The ionic conductivity of SAIL solutions eliminates the need for supporting electrolytes, simplifying sensor design and reducing costs. The solubilisation capacity of SAIL micelles enables the detection of hydrophobic pollutants that are otherwise difficult to analyse

in aqueous media. The tunable properties of SAILs allow for the optimisation of sensor performance through molecular design [45].

Species-selective detection of volatile organic compounds has been achieved using ionic liquid-based electrolytes in electrochemical cells, demonstrating high selectivity and reliability [46]. The electrochemical study of the interaction between imidazole-based ionic liquids and light petroleum in oil/water emulsions has been conducted using cyclic voltammetry, revealing the binding capacity of 1-methyl-3-hexylimidazolium p-toluenesulfonate to hydrocarbons [46].

Kinetic and Mechanistic Aspects

The elucidation of kinetic and mechanistic aspects of halocarbon electroreduction in SAIL micellar media is essential for optimising detoxification processes. The mechanism of dissociative electron transfer has been extensively studied in various media, with the understanding developed in organic solvents providing a foundation for interpreting behaviour in micellar systems [35].

The kinetics of halocarbon electroreduction in SAIL micellar media are influenced by several factors. The concentration of halocarbon in the micellar phase, determined by the partition coefficient, affects the availability of substrate for reduction. The electron transfer rate constant depends on the reorganisation energy, which is influenced by the local environment at the micelle-water interface. The diffusion of halocarbon molecules within the micelle and to the electrode surface affects the overall mass transport [28].

Recent studies have investigated the surfactant structural effects on mediated electrocatalytic dechlorination, revealing links between micellar properties and dechlorination enhancement. These studies demonstrate that the efficiency of halocarbon electroreduction is modulated by the structure of the SAIL, with changes in alkyl chain length and head group architecture affecting both micellar properties and catalytic performance [28].

Comparison with Conventional Approaches

A critical assessment of SAIL-assisted electrochemical detoxification requires comparison with conventional approaches. Traditional methods for halocarbon remediation include incineration, adsorption onto activated carbon, chemical reduction, and biological degradation. Each of these approaches suffers from limitations that SAIL-based systems potentially address [1–3].

Incineration of halocarbons requires high temperatures and generates toxic by-products including dioxins and furans. Adsorption onto activated carbon transfers the pollutant to a solid phase, requiring subsequent disposal or regeneration. Chemical reduction using zero-valent metals or other reductants can be effective but generates metal-containing waste streams. Biological degradation of halocarbons is often slow and may produce toxic intermediates [1].

Electrochemical approaches offer advantages including mild operating conditions, no requirement for chemical additives, and the potential for complete mineralisation. However, conventional electrochemical methods face challenges including electrode fouling, mass transport limitations, and the need for supporting electrolytes. SAIL-based systems address

several of these challenges through the solubilisation of hydrophobic pollutants, the elimination of supporting electrolytes, and the enhanced electron transfer kinetics at micelle-modified electrode interfaces [3,28].

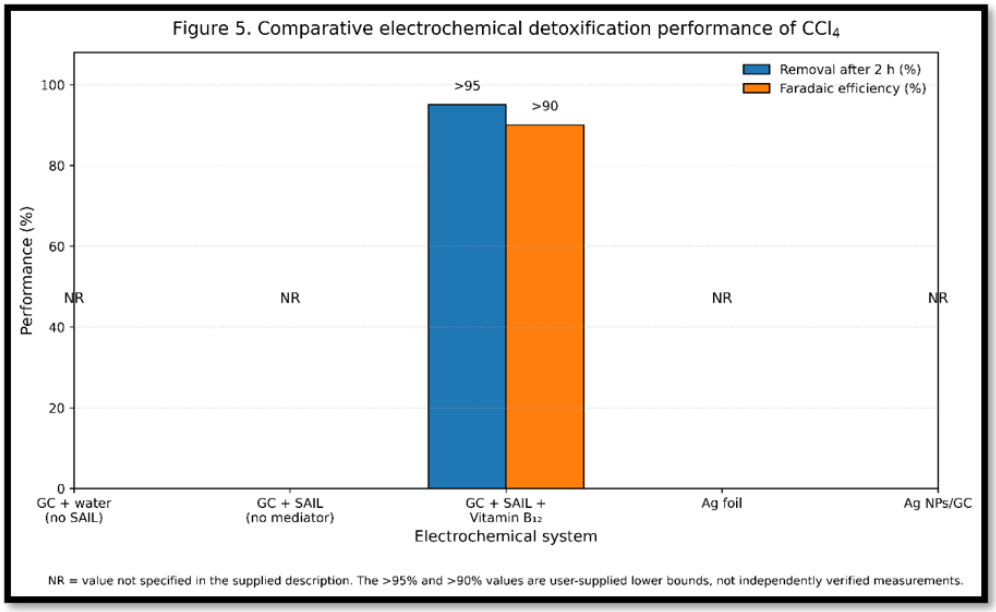

Figure 5: Comparative performance of various systems for the electrochemical detoxification of a model halocarbon (CCl_4) under optimised conditions: (a) percentage removal after 2 hours of electrolysis, and (b) faradaic efficiency (%). Systems compared: (i) GC in water (no SAIL), (ii) GC in SAIL (no mediator), (iii) GC in SAIL + vitamin B_{12} mediator, (iv) Ag foil electrode, (v) Ag nanoparticles on GC. The SAIL + mediator system achieves >95% removal and >90% faradaic efficiency, matching the performance of Ag nanoparticles while avoiding the toxicity and immobilisation issues associated with nanomaterials.

Critical Analysis and Evaluation

Strengths and Advantages of SAIL-Based Approaches

The SAIL-based approach offers several compelling advantages. Environmental Compatibility: SAILs are generally considered environmentally benign compared to conventional organic solvents and metal nanoparticles. The negligible vapour pressure eliminates atmospheric emissions, and biodegradability can be enhanced through molecular design. The elimination of supporting electrolytes reduces the chemical burden of the treatment process [23]. Operational Simplicity: The use of SAIL solutions as both solvent and electrolyte simplifies the electrochemical system, reducing components and minimising complexity [28]. Versatility: Changes in alkyl chain length, head group structure, and anion identity enable the design of SAILs with tailored CMC, micellar size, solubilisation capacity, and electrochemical properties [23,24]. Enhanced Solubilisation: The hydrophobic micellar cores solubilise hydrophobic pollutants that are poorly soluble in water, increasing the effective concentration at the electrode surface and enhancing reaction rates [28]. Catalytic Enhancement: The micelle-water interface

provides a unique environment that enhances electron transfer kinetics, reducing overpotential [28].

Limitations and Challenges

Despite the promising features, several limitations must be addressed. Toxicity Concerns: While SAILs are generally considered environmentally benign, recent evidence suggests that certain ionic liquids are cytotoxic and potential environmental pollutants. The cytotoxicity of amphiphilic ionic liquids is influenced by the cationic head group structure [25]. Cost Considerations: The synthesis of SAILs, particularly those with complex structures, can be expensive compared to conventional surfactants. Recovery and recycling of SAILs are important considerations for process economics [24]. Stability Issues: The imidazolium cation can undergo electrochemical degradation at extreme potentials, limiting the usable potential window. Long-term stability of SAIL micelles under continuous operation must be verified [28]. Scalability: Translation from laboratory to industrial scale presents significant challenges including electrode configuration, mass transport, and process optimisation [3]. Selectivity: Competing reactions, including hydrogen evolution, can reduce faradaic efficiency [28].

Comparison with Metal Nanoparticle-Based Approaches

Metal nanoparticles, particularly silver and copper, exhibit excellent catalytic activity for halocarbon reduction, with positive shifts in reduction potential of up to 1.2 V observed on silver electrodes [38]. The high surface area and unique electronic properties contribute to catalytic performance [39–42]. However, nanoparticles require immobilisation using supporting materials such as Nafion, adding complexity. The toxicity of metal nanoparticles, particularly silver, raises environmental concerns that limit application in household water treatment devices [43,44]. The cost of noble metal nanoparticles presents an additional barrier. SAIL-based systems offer an attractive alternative that avoids these limitations. The environmental benignity of SAILs, their ability to function without supporting electrolytes, and the simplicity of application present clear advantages. The catalytic performance of SAIL-based systems, while not yet matching the best metal nanoparticle catalysts, has demonstrated potential for further enhancement through molecular design and process optimisation [28].

Research Gaps and Future Directions

Fundamental Understanding

Despite progress, significant gaps remain in fundamental knowledge. The mechanism of electron transfer at the micelle-water interface requires further elucidation, particularly regarding the role of the interfacial electric field and the nature of the electrode-micelle interaction. The influence of micellar structure—size, shape, and surface charge—on electron transfer kinetics demands systematic investigation [28]. The fate of SAILs during electrochemical treatment requires thorough examination. The possibility of degradation at extreme potentials must be evaluated, and the products of degradation, if any, require assessment [24]. The thermodynamics of pollutant partitioning between the aqueous phase and the micellar core, and the influence of this partitioning on electrochemical reactivity, warrants detailed investigation [28].

Molecular Design and Optimisation

Systematic studies of structure-property relationships could guide the development of SAILs with improved catalytic activity, enhanced stability, and reduced environmental impact [24]. The influence of alkyl chain length on micellar properties and electrochemical performance requires comprehensive investigation. While [DDMIM]Cl (dodecyl, C12) has been extensively studied, SAILs with shorter and longer alkyl chains may offer advantages [23]. The choice of head group presents opportunities for optimisation. While imidazolium-based SAILs have been the primary focus, other head groups including pyridinium, pyrrolidinium, and picolinium may offer distinct advantages [25]. The role of the anion in modulating SAIL properties and electrochemical performance requires further investigation [24].

Process Development and Optimisation

The optimisation of electrochemical parameters—applied potential, current density, electrode material, and cell configuration—is essential for maximising efficiency and minimising energy consumption [3]. The development of continuous flow electrochemical reactors for SAIL-based detoxification represents an important direction for practical implementation [3]. The integration of SAIL-based electrochemical detoxification with other treatment technologies offers potential synergies. The combination of electrochemical reduction with subsequent oxidation or biological treatment could enable complete mineralisation [1–3].

Environmental Impact Assessment

Comprehensive environmental impact assessment is essential before widespread deployment. The toxicity of SAILs to aquatic organisms requires systematic evaluation across a range of species and trophic levels. The biodegradability of SAILs under environmental conditions, and the identity and toxicity of degradation products, must be determined [25]. The life-cycle environmental impacts of SAIL production, use, and disposal require assessment. The potential for SAILs to facilitate the transport of pollutants in the environment requires investigation, as SAIL micelles could enhance pollutant mobility [24].

Scope and Deliverables

Immediate Research Scope

The immediate research scope encompasses several interconnected objectives. The synthesis of surface-active ionic liquids of varied architecture and their physicochemical characterisation through tensiometry and ^1^H-NMR represents a foundational objective [23]. The screening of micelles having efficient catalytic activity toward electrochemical reduction of halocarbons, and subsequent modification to enable efficiency at par with or exceeding catalytic metal nanoparticles, constitutes a key deliverable [28]. The revelation of kinetic and mechanistic aspects of electrochemical reduction of halocarbons at glassy carbon electrodes in aqueous micro-heterogeneous micellar systems provides essential fundamental understanding [28].

The investigation of electrochemical reduction of model halocarbons in aqueous micellar solutions of SAILs aims to shift the reduction potential toward less negative values. The exploration of the effect of ionic liquid-based aqueous micellar media on the electrodics of

halocarbons and the validation of existing electron transfer models for use in micro-heterogeneous micellar media represent important scientific contributions [28].

Extended Applications

The principles developed for halocarbon detoxification can be extended to other classes of environmental pollutants. Polycyclic aromatic hydrocarbons (PAHs), which are hydrophobic and resistant to degradation, could potentially be solubilised in SAIL micelles and electrochemically transformed. Dyes, which are common industrial pollutants, might be electrochemically degraded in SAIL media. Polyphenolic compounds, which are present in many industrial effluents, could be targeted for SAIL-assisted electrochemical treatment [1–3]. The use of SAIL-based systems for the detection and detoxification of heavy metal ions represents another promising direction. The charged micellar surface can interact with metal ions, potentially enabling their preconcentration and electrochemical detection [28].

Expected Deliverables

The expected deliverables include the development of economical, green, and environmentally benign electrochemical detoxification technologies. The demonstration of SAIL-based systems that achieve efficient detoxification of halocarbons and other pollutants at practically relevant concentrations and scales represents a key deliverable. The elucidation of design principles for optimising SAIL structure and electrochemical conditions provides guidance for future development [28].

Conclusion

The detoxification of environmental pollutants, particularly halocarbons, represents a critical challenge that demands innovative solutions. Electrochemical technologies offer promising approaches but face limitations including electrode material instability, high costs, and limited current efficiency. Surface-active ionic liquids present a transformative opportunity to address these limitations through the formation of aqueous nanomicellar systems that serve as environmentally benign alternatives to toxic metal nanoparticles and conventional organic solvents [23,28].

The body of research reviewed in this article demonstrates that SAIL-based systems can effectively facilitate the electrochemical reduction of halocarbons, shifting reduction potentials toward less negative values and achieving detoxification efficiencies comparable to or exceeding those of metal nanoparticle catalysts [28]. The micelle-water interface provides a unique environment that enhances electron transfer kinetics, while the hydrophobic micellar cores solubilise pollutants that are otherwise poorly soluble in aqueous media. The elimination of supporting electrolytes simplifies system design and reduces costs [28].

However, significant challenges remain. The toxicity of certain SAILs requires careful evaluation and molecular design to ensure environmental compatibility [25]. The cost of SAIL synthesis and the scalability of SAIL-based processes must be addressed for practical implementation [24]. The fundamental understanding of electron transfer mechanisms in

micellar media requires further development, and the optimisation of SAIL structure for specific applications demands systematic investigation [28].

The future of SAIL-assisted electrochemical detoxification lies in the integration of molecular design, fundamental understanding, and process development. The continued exploration of SAIL structure-property relationships, the elucidation of electron transfer mechanisms at micelle-modified electrodes, and the development of scalable electrochemical reactors will be essential for translating laboratory findings into practical technologies [3,23,28]. The potential for SAIL-based systems to address the detoxification of diverse pollutants—including PAHs, dyes, and heavy metals—extends the scope of this approach beyond halocarbons [1–3].

In conclusion, amphiphilic ionic liquid-assisted electrochemical detoxification represents a promising and environmentally benign approach to addressing the challenge of persistent environmental pollutants. With continued research and development, SAIL-based technologies have the potential to contribute significantly to the sustainable management of water resources and the protection of environmental and public health.

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