Ionic liquid membranes for the separation of phenols, metals, drugs and other compounds from aqueous media: A review of new developments

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ABSTRACT

Liquid membranes are an effective method for the separation of various chemical materials in aqueous media. Ionic liquids have emerged in recent years as environmentally friendly alternative solvents for separation processes. The remarkable features of ionic liquids like negligible vapor pressure, high stability, liquid at room temperature, tunable structure and properties, and versatile operations have rapidly spiked research on the application of ionic liquids to various membranes processes. They are therefore potential solvents to design novel advanced separation processes. In this regard, liquid membranes based on ionic liquids, denoted as ionic liquid membranes, emerge as a strong contender. This paper focuses on the possibility of separating various materials using ionic liquid membranes and provides insights of ionic liquid membrane applications for various chemical separations. Ionic liquid membranes have been used lately for the separation of various chemical compounds from aqueous media, such as phenols, drugs, metals, dyes, amino acids, carboxylic acids, pesticides, hydrocarbons, and gas mixtures. They resulted in a very high percentage removal (up to 99.5%) from aqueous solutions. It was concluded that the hydrophobic effect and the hydrogen bond of ionic liquids play an important role in the separation performance. These results will also contribute to the choice of ionic liquids for higher removal efficiency and the design of novel ionic liquid membranes for specific target substances.

Keywords: Liquid membrane, ionic liquids, separation, aqueous media.

1. Introduction

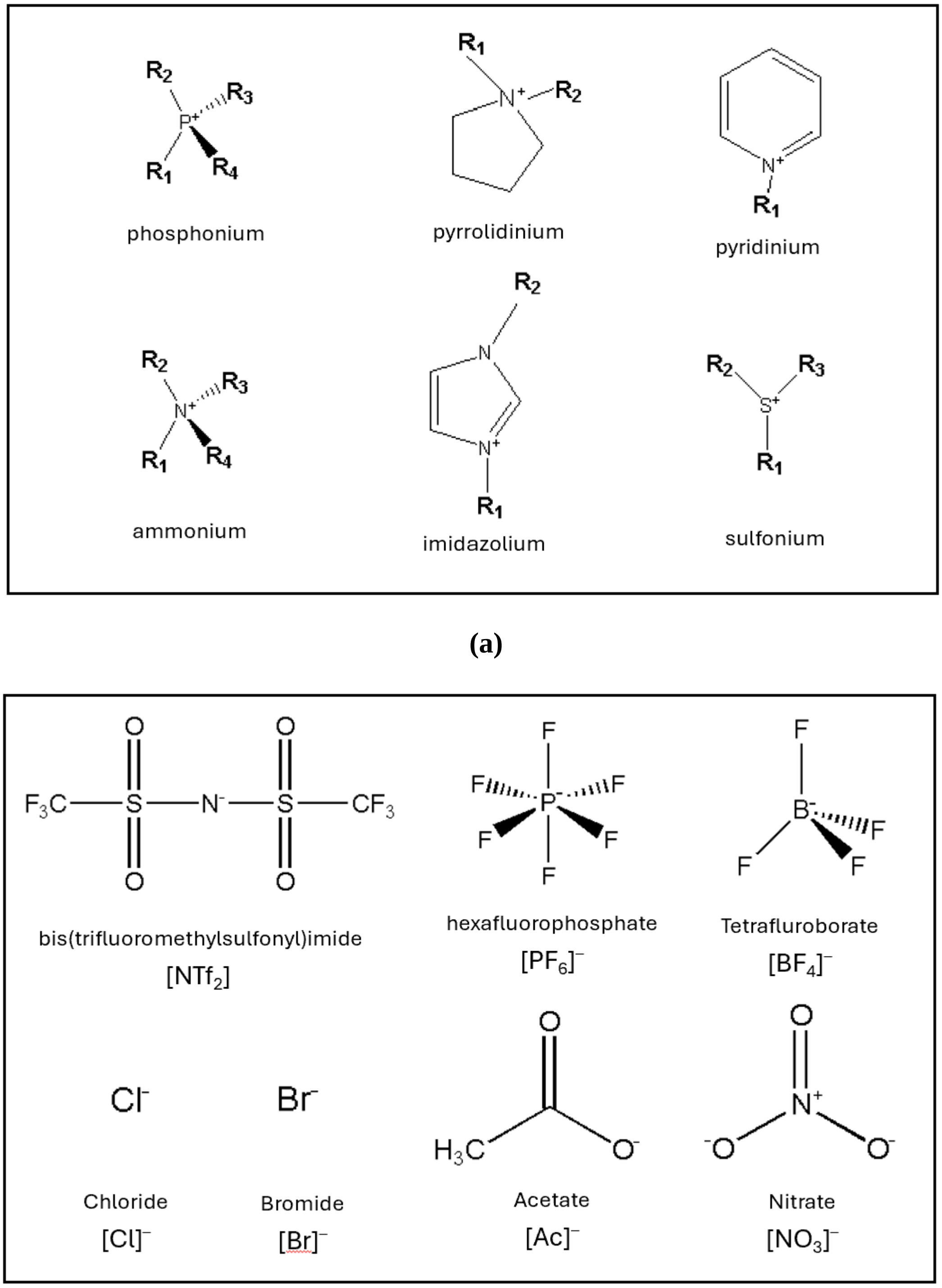
Ionic liquids have emerged as environmentally friendly alternative solvents in recent years. They are promising candidates to replace conventional organic solvents due to their remarkable properties like their low vapor pressure, non-flammability, thermal stability, safe preparation and handling, recyclability, as well as their tunable structure and properties. Due to their negligible vapor pressure (near zero), they do not pose an inhalation risk during usage as in the use of conventional volatile organic solvents. Based on these significant features of ionic liquids, they are also classified as green solvents [1,2].

Ionic liquids are a novel group of solvents formed by the combination of certain anions and cations. The term ionic liquid is used for organic salts that melt below 100 °C. When the melting point is below room temperature, an ionic liquid (IL) is denoted as a room-temperature ionic liquid (RTIL) [3,4]. Physicochemical features of ionic liquids can be tailored to perform particular chemical tasks by suitable choice of cations and anions [5]. The structures of the cations and anions commonly used to synthesize ionic liquids are shown in Figure 1. The cations are organic-based like pyrrolidinium, phosphonium, pyridinium, ammonium, imidazolium, and sulfonium. The anions can be either organic or inorganic-based, like bis(trifluoromethylsulfonyl)imide, hexafluorophosphate, tetrafluoroborate, chloride, acetate, bromide, nitrate, and halides, among others. The anion ascertains the hydrophobic characteristic of the ionic liquid [6,7]. Multiple anion/cation combinations form more than 10^6 different ionic liquids, each having specific physicochemical features [8]. By tuning the combination of different cations and anions and by understanding the ions charge transfer mechanism and the dissolution state, ionic liquids with different properties can be designed. Thus, compared to conventional organic solvents, ionic liquids can gain unlimited structural properties that can be used in special applications. This makes them effective designer solvents [9]. Besides, they exhibit a wide range of solubility of inorganic and organic compounds and a wide electrochemical window unlike conventional solvents [5]. The improved solvent properties of ionic liquids have rapidly spiked research on the application of ionic liquids to separation, catalysis, synthesis, and production processes [10–12]. To further expand the applications, bio-ionic liquids (bio-ILs) have been developed in recent years. These novel ionic liquids involve anion and cation groups derived from bio-organic molecules such as amino acids, organic acids and glucose. Bio-ionic liquids are increasingly used for sustainable pharmaceutical, biomedical, and food applications due to the advantages they offer in terms of easy biodegradability, biocompatibility, their abundance, relatively environmentally friendly behavior and low cost compared to traditional ionic liquids [13–16]. Besides, Santiago et al. [16] evaluated bio-ionic liquids as promising solvents in classical industrial separation processes such as liquid-liquid extraction (recovery of value-added compounds or contaminants from aqueous media, hydrocarbon separation, desulfurization and denitrogenation), gas absorption (NH_3, H_2S, CO_2, acetone or refrigerants) using COSMO-RS. They reported that some bio-ionic liquids showed competitive performance compared to common ionic liquids. They also emphasized future studies should be performed to find hydrophobic bio-ionic liquids that can be used in separation processes.

There are many traditional methods reported for the separation and purification of substances from aqueous media or reaction medium like adsorption [17,18], extraction [19,20], distillation [21,22], ion exchange [23–25], nanofiltration [26–28] and ultrafiltration [29,30], reverse osmosis [31,32], coagulation and flocculation [33,34], electrodialysis [35,36], and precipitation [37,38]. However, there is a great demand for novel or improved technology that can compete with traditional separation processes [5]. In recent years, one of the developing and promising techniques proposed as an alternative to conventional separation processes is liquid membrane technology. Liquid membranes are becoming increasingly attractive due to their high separation efficiency, high selectivity, ease of use, low energy requirement, and low construction and operation costs [39,40]. Additionally, the extraction and stripping steps are combined into one stage in liquid membrane processes; the high interfacial area for mass transfer ensures a high efficiency [41]. The extraction step is essentially the same as in a liquid–liquid extraction process, but the transport is controlled by kinetics rather than equilibrium parameters. Thus, it is governed by nonequilibrium mass transfer characteristics where the separation is not limited by the equilibrium conditions [42,43]. Basically, the liquid membrane is formed by an organic liquid phase between two aqueous phases. In this three-phase technique, solutes are extracted from an aqueous solution through an organic liquid phase into another aqueous phase [43]. Due to these superior benefits over liquid–liquid extraction and solid membranes, liquid membranes are used in the separation and concentration of various materials in diverse fields like textile, food, biotechnology, medicine, hydrometallurgy, and environmental protection [44].

Over the last decade, ionic liquids combined with liquid membranes have become a promising novel approach for separation processes. In this way, the solvent properties of ionic liquids contribute to raise the membrane separation performance [8]. Liquid membranes are denoted as ionic liquid membranes (ILMs) when an ionic liquid is used in a liquid membrane [45]. They can be used for the facilitation of catalytic reactions (Friedel Crafts, Heck reactions, hydroaminations, or hydrogenation etc.), the separation of different compounds (hydrocarbons, organic acids, metals, or gases etc.), and the fabrication of advanced electrochemical devices (sensors, solar cells, fuel cells or lithium batteries etc.). Due to the unique properties of ionic liquids, ionic liquid membranes are more stable compared to conventional liquid membranes based on organic solvents [5]. Ionic liquids can be utilized directly as raw materials to prepare liquid membranes [46]. The use of an ionic liquid as a membrane phase is becoming increasingly attractive as an alternative to traditional separation techniques [40,45].

liquids.



(a)

(b)

Figure 1. The structures of **(a)** cations and **(b)** anions commonly used to synthesize ionic liquids.

This paper reviews the use of ionic liquid membranes for the separation of various compounds in aqueous or reaction media. A number of recent studies on ionic liquid membranes have been compiled. The aim of this study is to assess the current status, developments, and further needs of ionic liquid-based membrane technologies. By targeting ionic liquids in separation processes, different type of liquid membranes such as bulk liquid membranes (BLMs), supported liquid membranes (SLMs), emulsion liquid membranes (ELMs), and ionic liquids in BLMs, SLMs, and ELMs, e.g., bulk ionic liquid membranes (BILMs), supported ionic liquid membranes (SILMs), emulsion ionic liquid membranes (EILMs) are highlighted in this paper. This review provides an overview of the ionic liquid-based membrane technologies and their performance for the separation of various target materials. It is expected to contribute to the design of innovative ionic liquid-based liquid membranes for various separation processes in different areas.

2. Ionic liquids in separation processes

The combination of ionic liquids and separation processes is of growing interest, as it increases efficiency in the selective recovery and removal of many different substances such as carboxylic acids [1,3,6,11,40,45,47–53], metals [54–59], drugs [60], phenolic compounds [54,61–66], amino acids [67], gases [68–70], hydrocarbons [71–73], pesticides [74,75], and dyes [54,76–79] from different media. In consequence of their unique properties as explained above, ionic liquids appear as green designer solvents that can replace traditional organic solvents in separation processes. The use of traditional organic solvents in the separation processes brings some problems such as volatility, flammability, and toxicity properties, causing environmental, health, and safety problems [80].

One of the attractive aspects of ionic liquids is their tunability. Their chemical and physical features, like viscosity, density, solubility, and melting point can be controlled by selecting dissimilar cations and anions, and they can be tailored for specific applications. In that context, ionic liquids are also recognized as “designer solvents” [39,81]. As a consequence, it is possible to choose ionic liquids with better extraction efficiencies and thermodynamic properties.

The applicability of ionic liquids in separation methods for the removal and purification of various substances is a research area that is of interest and open to development. Ionic liquids can be used in various roles: as extractant, diluent, or electrolytic medium in separation processes [82]. Besides, ionic liquids modified materials are used as adsorbents due to their excellent separation performance [83–87]. Table 1 shows a summary of separation studies reported in the literature that use ionic liquids to separate various target materials from different media. As can be seen in Table 1, ionic liquids are extensively used in solvent extraction for the separation of various substances such as phenolic compounds [61–64], amino acids [67], antibiotics [60], metals [56–59], hydrocarbons [71–73], carboxylic acids [47–50,52,53,88–90], pesticides [74,75] and dyes [76,77,79] from diversified media. Thasneema et al. [54] investigated the extraction of As, Cu, Cr, Cd, Pb, Hg, and Zn from their standard solutions, textile dyes such as methyl orange, methylene blue, malachite green, Congo red, and alizarin red S from aqueous solutions and phenolic compounds from cashew and rice industrial wastewater by using phosphonium-based liquids. They found that ionic liquids have a broad ability for the separation of heavy metals, dyes, and phenolic compounds.

Ionic liquids are generally biocompatible as they do not inactivate enzymes and thus ensure the structural integrity of the biomolecules and can be also used in the removal of biomolecules from natural sources and fermentation media [91]. Other types of solvent extraction methods utilized for the extraction of materials include two-phase extraction, reverse micellar extraction, and reactive extraction. Ionic liquids are used directly as conventional organic solvents replacements in solvent extraction, and they are also used by formed ionic liquid-based aqueous biphasic systems (two-phase extraction systems) by adding salting-out agents to aqueous solutions of hydrophilic ionic liquids [60,91]. In classical reactive extraction, tributyl phosphate

(TBP), and trioctyl phosphine oxide (TOPO) as neutral organophosphorus extractants, di-2-ethylhexyl phosphoric acid (D2EHPA) as an acid extractant, and trioctylamine (TOA), tributylamine (TBA), and tridodecylamine (TDA) as long-chain amines, are widely preferred as extractants [92–94]. Recently, ionic liquids are considered as greener alternative to the amines as extractants in reactive extraction of carboxylic acids. Marták and Schlosser [51] investigated ionic liquids in dodecane as extractants for the reactive extraction of lactic acid. They found that the phosphonium ionic liquid Cyphos IL-104 was an effective extractant for lactic acid extraction with considerably higher distribution coefficients above 40. They also reported that the distribution coefficients of the classical C_8–C_{10} trialkylamines were approximately 1. The synergistic effect of the anion of the ionic liquid was mainly responsible for achieving the higher distribution coefficient of lactic acid with Cyphos IL-104. Apart from this, phosphonium, ammonium and imidazolium ionic liquids showed a good performance as reactive extractants of butyric and lactic acids extraction in previous studies by Marták and Schlosser [49,50,95,96]. Ionic liquids are also used in applications such as carbon dioxide capture [97], gas separation [98], extractive distillation [71,72] and biomass dissolution [99,100]. For carbon dioxide capture, traditional amine-based solvents are widely used. However, amines react with carbon dioxide and the desorption process is relatively difficult, and amine solvents are volatile and corrosive, thus resulting in a high desorption cost and environmental damage. Therefore, there is a need to develop novel clean technologies that use less energy for the regeneration to replace traditional amine solvents [97,101]. Recently, ionic liquids have been proposed as alternative sorbents to capture carbon dioxide, and for this purpose, carbon dioxide solubility in different ionic liquids has been investigated. Ayad et al. [97] investigated carbon dioxide solubility in tricyanomethanide-based ionic liquids consisting of imidazolium, pyrrolidinium, and pyridinium cations. They observed that a high carbon dioxide solubility in ionic liquids was achieved at low pressure and the highest solubility was obtained in pyridinium cation. Zhang et al. [102] screened potential ionic liquids for carbon dioxide capture and separation. In a preliminary screening, 76 conventional ionic liquids were evaluated in terms of carbon dioxide working capacity and carbon dioxide dissolution enthalpy from Henry's law constant. Afterwards, 17 selected ionic liquids having carbon dioxide working capacities higher than 0.1 g CO_2/g ionic liquids and carbon dioxide dissolution enthalpies lower than 15 kJ mol^{-1} were screened in terms of energy consumption. In the final screening, the energy consumptions of seven ionic liquids including [Emim][NTf_2], [Bmim][NTf_2], [Bmim][BF_4], [Bmim][PF_6], [Hmim][NTf_2], [Bmpy][NTf_2], and [Hmpy][NTf_2] were calculated using the carbon dioxide working capacity from measured the carbon dioxide solubility. Among these ionic liquids, [Hmpy][NTf_2] had the lowest energy consumption with the value of 0.991 GJ.tonCO_2^{-1}, while [Bmpy][NTf_2] had the highest energy consumption of 1.355 GJ.tonCO_2^{-1}. Additionally, the values of energy consumption of these ionic liquids were compared with those of commercial CO_2 adsorbents such as traditional amines (monoethanolamine and methyldiethanolamine), and dimethyl ethers of polyethylene glycol. The results demonstrated that the energy consumptions of the seven screened ILs were lower than those of the commercial CO_2 absorbents. It was also reported that the screened ionic liquids can be used as potential adsorbents for carbon dioxide capture and separation. Gouveia et al. [98] also investigated mixed of H_2, CO_2 and N_2 gas separation using poly(ionic liquid)–pyrrolidinium based ionic liquid (PIL-IL) membranes with $[NTf_2]^-$ and $[C(CN)_3]^-$ anions. They found that a PIL $C(CN)_3$–60 IL $C(CN)_3$ membrane had the best mixed separation performance with a CO_2/H_2 permselectivity of 11.4 and a CO_2 permeability of 324.7 Barrer even at the highest temperature and feed pressure (T =80 °C and P_{feed} =4 bar). In extractive distillation, ionic liquids are proposed as mass separating agents for the removal of hydrocarbon mixtures [71,72]. Organic compounds such as N-methylpyrrolidone, sulfolane, and N-formylmorpholine, are used as mass separating agents in conventional extractive distillation methods. These mass agents have several disadvantages like volatility, flammability, and toxicity, leading to adverse environmental effects. Conventional extractive distillation methods have high operating costs and energy requirements due to the often high boiling points and losses of solvents. Therefore, choosing the appropriate solvent is a very important stage to ensure an economical, effective, and sustainable extractive distillation method [72]. Recent studies in the literature on the use of ionic liquids in other separation processes provided helpful insights, but they are still limited and there is still a gap in the knowledge needed to develop and optimize alternative separation methods [103].

Im et al. [99] explored the use of ionic liquids such as [Bmim]Cl, [BMMor]Cl, [BMPip]Cl, and [DMIM][MP] to dissolve cellulose, hemicellulose, and lignin biomass as an alternative to highly toxic organic solvents. The biomass regenerated after treatment with ionic liquids, and then the structural and thermal properties of cellulose, hemicellulose and lignin were examined. The results of this study indicated that the use of ionic liquids could increase the application of biomass in various fields. Yang et al. [100] used ionic liquid [Bmim][Cl] to dissolve lignin, hemicellulose, and cellulose from corn stalks and prepare cellulose fibers. It was found that the hemicellulose was completely removed, the lignin removal was 92.35%, and the cellulose removal was 85.32% after the corn stalk was dissolved at 150 ℃ for 11.5 h with an arginine mass fraction of 2.5%. This method significantly simplifies the preparation of cellulose fibers from corn stalks, and it is environmentally friendly and sustainable.

Table 1. Summary of the use of ionic liquids in various separation techniques.

Target Substance		Separation method	Ionic liquid composition	Ref.
Phenolic compounds	Phenolic compounds from different bio-oils obtained by lignin pyrolysis	Solvent extraction	[Ch][NTf_2] as a solvent	[62]
	Phenolic compounds from hexane as the model oil		[ABZIM]Cl, [DBZIM]Cl, [BZVIM]Cl as solvents	[64]
	Phenol and 2,4-dichlorophenol in aqueous media		[P_{66614}][$C_9H_{19}COO$], [P_{66614}][(i-C_8)POO] as solvents	[63]

	2,4-dichlorophenol in aqueous solution	Adsorption	[P$_{66614}$][C$_9$H$_{19}$COO] immobilized in sodium alginate as an adsorbent	[86]
Amino acids	L-tryptophan, L-phenylalanine, L-tyrosine, L-leucine, D-valine from aqueous media	Solvent extraction	[Bmim][PF$_6$],[Hmim][PF$_6$],[Hmim][BF$_4$], [Omim][BF$_4$] as solvents	[67]
Antibiotics	Amoxicillin and ampicillin in buffered solution	Two-phase extraction	[Omim][BF$_4$] as a solvent	[60]
Metals	Rhenium in aqueous solution	Solvent extraction	[Bmim][NTf$_2$], [Omim][NTf$_2$] as diluents, TOA and Alamine 336 as extractants	[80]
	Cobalt and nickel in aqueous solution		[P$_{66614}$]Cl as diluent	[104]
	Lead in aqueous solution		[C$_6$byp][Tf$_2$N] as solvent	[57]
	Lead in water and food samples	Micro-solid phase extraction	Sepabeads SP70 resin impregnated with [Bmim][PF$_6$]	[105]
	Gold-thiosulfate complex in aqueous solution	Adsorption	Butylimidazolium-based ionic liquids modified chitosan as adsorbents	[83]
Rare earth ions	Neodymium and dysprosium from NdFeB magnet or leaching solution	Solvent extraction	[P$_{66614}$][NO$_3$] as solvent, EDTA as a complexing agent	[106]
	Scandium(III) from rare earth elements aqueous solutions		[N333 MeOAc][Tf$_2$N] and [N444 MeOAc][Tf$_2$N] diluted in chloroform	[107]
Carboxylic acids	Lactic, malic, and succinic acids from dilute aqueous solutions	Solvent extraction	[P$_{66614}$][Cl], [P$_{66614}$][C$_9$H$_{19}$COO], and [P$_{66614}$][[(i-C$_8$)POO] as extractants	[88]
	Butyric acid in aqueous solution		[C$_n$C$_n$C$_n$C$_1$N][BTMPP] as an extractant and its dodecane (as a diluent) solution.	[52]
	Acrylic acid in aqueous solution	Solvent and reactive extraction	[Bmim][NTf$_2$],[Hmim][NTf$_2$], [Bmim][PF$_6$], [Hmim][PF$_6$] as diluents and TBP as an extractant	[45]
	Glutaric acid in aqueous solution			[48]
	Valeric acid in aqueous solution			[47]
	Propionic acid in aqueous solution			[1,3]
	Vitamin C (ascorbic acid) from 2-ketogluconic acid in aqueous solution		[P$_{66614}$][(i-C$_8$)POO], [P$_{66614}$][C$_9$H$_{19}$COO], [Bmim][PF$_6$], [Hmim][PF$_6$], [Omim][PF$_6$] as the extractants and heptane and octanol as the diluent	[108]
Dyes	Methylene blue in aqueous solution	Solvent extraction	[Bmim][NTf$_2$], [Hmim][NTf$_2$], [Omim][NTf$_2$], [BnMIm][NTf$_2$], [HPhIm][NTf$_2$] as solvents	[79]
	Methyl blue and methyl orange in aqueous solution		[N$_{1888}$][SCN], [N$_{1888}$][DCA], [N$_{1888}$][BA], [N$_{1888}$][Hex] as solvents	[76]
	Congo red in aqueous solution	Adsorption	[Bvim][Br] modified magnetic cellulose/sepiolite composite	[84]
Hydrocarbons	hexene/ hexane mixture cyclohexene/cyclohexane mixture	Solvent extraction	[Emim][NTf$_2$],[Emim][DCA], [Emim][TCM] as solvents	[73]
	Benzene, toluene, and xylene from pyrolysis gasoline	Extractive distillation	[Emim][TCM], [B4mpy][TCM] as mass agents	[72]
	n-hexane/1-hexene mixture		[B4mpy][TCM],[E4mpy][NTf$_2$], [B4mpy][NTf$_2$],[Emim][DCA], [Emim][SCN],[Emim][TCM], [Emim]$_2$[Co(SCN)$_4$], [Bmim]$_2$[Co(SCN)$_4$], [P$_{66614}$][DCA], [P$_{66614}$][DCA] as mass agents	[71]
	n-heptane/toluene mixture		[B4mpy][TCM],[B4mpy][NTf$_2$], [E4mpy][NTf$_2$],[Emim][DCA], [Bmim][DCA],[Emim][SCN], [Bmim][SCN],[Emim][TCM], [Bmim][TCM] as mass agents	[109]
Organic compounds	n-propanol/n-propyl acetate azeotropic mixture	Extractive distillation	[Dmim][Ac], [Omim][Ac], and [Hmim][Ac] as entrainers	[110]
	methanol - dimethyl carbonate azeotropic mixture		[Bmim][Tf$_2$N] or [Emim][Tf$_2$N] or [Emim][PF$_6$] as entrainers	[111]

3. Ionic liquids in Liquid Membranes

Liquid membranes (LMs) include three types: bulk liquid membranes (BLM), supported liquid membranes (SLM), and emulsion liquid membranes (ELM) [112,113]. Each type of LM consists of an organic membrane phase (M), a liquid feed phase (F, feed or donor phase), and a liquid stripping phase (S, stripping or receiving phase). The aqueous feed phase contains the target component. The target component (solute) is transported from the feed phase through the membrane phase and is released into the stripping phase. Solute transport in liquid membranes is primarily based on the solution-diffusion mechanism, where solutes dissolve in the liquid membrane and diffuse through the liquid membrane due to a concentration gradient [114]. A schematic representation of liquid membrane technologies is also given in Figure 2. The use of a liquid membrane based on ionic liquids (ILM) is a promising separation technology for various chemical substances from different media; this is explained in the next section.

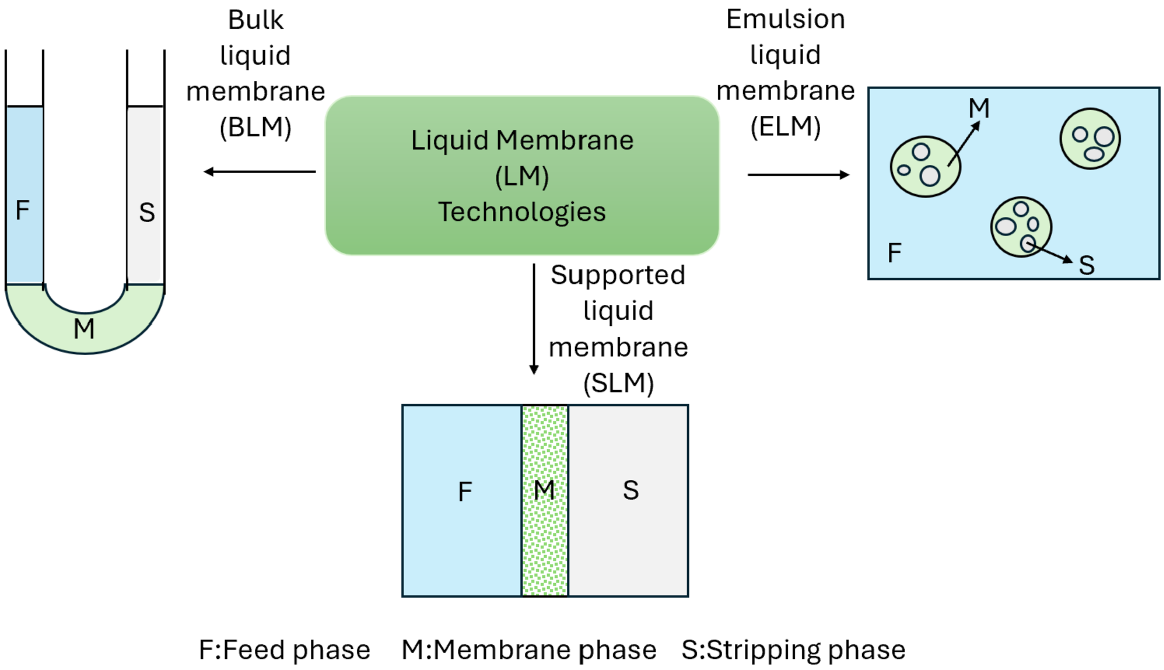
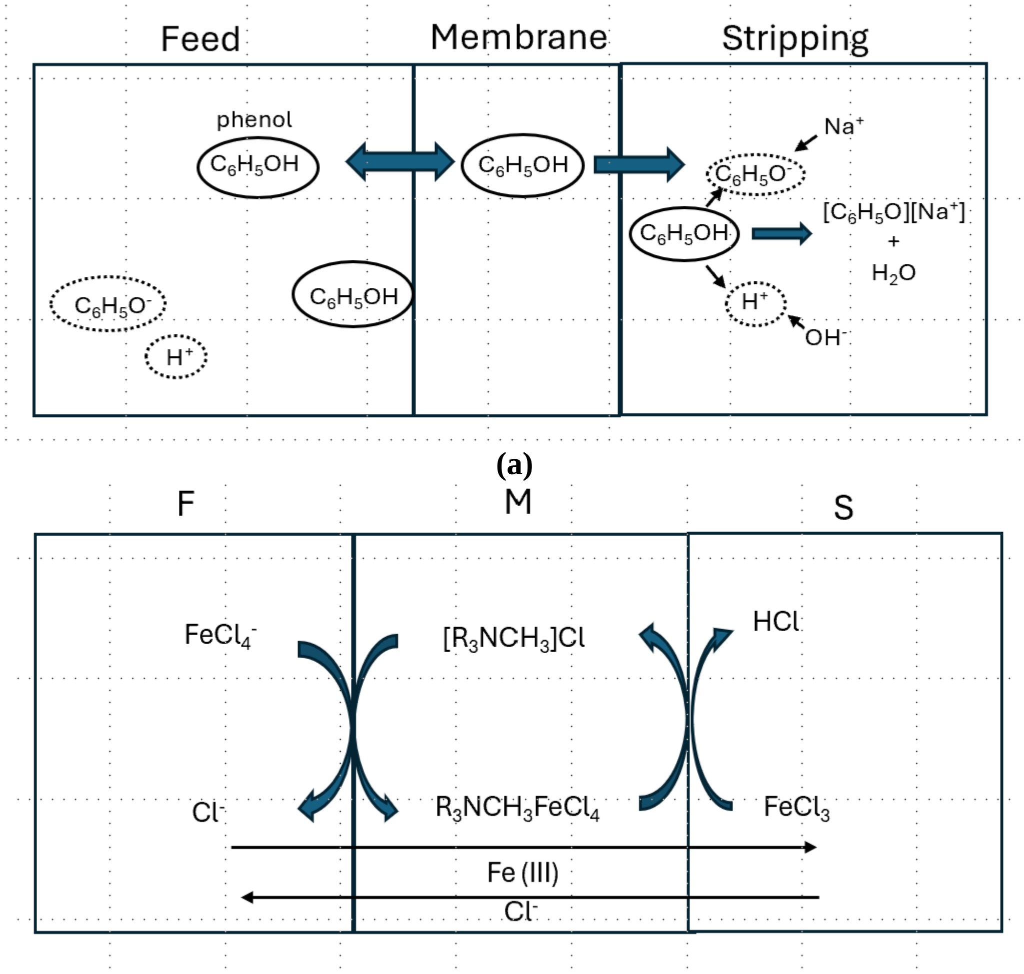


Figure 2: Schematic representation of liquid membrane technologies.

3.1. Bulk liquid membranes

Bulk liquid membranes (BLMs) are liquid membranes consisting of a bulk liquid membrane phase (M), a liquid feed phase (F, feed or donor phase), and a liquid stripping phase (S, stripping or receiving phase). The aqueous feed and stripping phases come into contact with the immiscible liquid membrane phase. The BLM separates by taking advantage of the differences in diffusion and solubility between liquid phases [6,11]. BLMs have many advantages such as ease of use, low operating cost, and simultaneous separation and enrichment processes. Nevertheless, a BLM has notable disadvantages as well: contamination of the feed by the solvent, membrane entrainment during extraction, and frequent emulsification on the LM surface, limiting its industrial potential [115].

The use of an ionic liquid as the membrane phase in BLM is receiving growing interest and is denoted as 'bulk ionic liquid membrane' (BILM) [40]. Table 2 reports BLM and BILM studies on the separation of various compounds from aqueous solutions. The literature review in Table 2 indicates that conventional organic solvents such as toluene, benzene, kerosene, xylene, chloroform, and dodecane are widely used as membrane phases. BILM studies are very limited, so far it has been reported in the separation of phenols [66,116,117], amino acids [118], metal [119], and carboxylic acids [6,11,40,45,120]. Ng et al. [66] investigated the technical feasibility of ionic liquids as BILMs for phenol removal. They used ionic liquids with high hydrophobicity, [Bmim][FAP], [Bmim][PF_6], and [Bmim][NTf_2]. They found that [Bmim][NTf_2] had the highest phenol removal with the extraction efficiency of 96.21% and stripping efficiency of 98.10%. They also clarified the transport mechanism of phenol in [Bmim][NTf_2] through BILM as illustrated in Figure 3(a). Among the tested ionic liquids [Bmim][NTf_2] has the highest hydrogen bond basicity strength and the lowest viscosity. The extraction efficiency was found to be more dependent on the hydrogen bond basicity strength of ionic liquids. Additionally, the stripping efficiency varied depending on the viscosity of the membrane solvent. For all the ionic liquids studied, a good membrane stability and reusability of the ionic liquids were obtained. Chasib et al. [117] also tested high hydrophobicity ionic liquids, [Emim][NTf_2], [Bmim][NTf_2], [Bmim][PF_6], [Hmim][PF_6], and binary mixtures of these ionic liquids for the separation of phenol and other phenolic compounds from the industrial effluents. They noticed that the structures of both phenolic compounds and ionic liquids had a significant impact on the extraction efficiency. The extraction efficiencies were ordered depending on the increasing the strength of hydrogen bond basicity, *i.e.* [Bmim][NTf_2] (0.24) > [Emim][NTf_2] (0.23) > [Hmim][PF_6] (0.22) > [Bmim][PF_6] (0.21). The highest extraction efficiency was obtained 91% for [Bmim][NTf_2]. Moreover, binary mixtures of [Bmim][NTf_2+PF_6] gave the highest extraction efficiency of 98.5%. The stripping efficiencies were changed depending on the viscosity of ionic liquids, *i.e.* [Emim][NTf_2] (37 cP) > [Bmim][NTf_2] (52 cP) > [Bmim][PF_6] (450 cP) > [Hmim][PF_6] (585 cP). In the BLM process, the membrane solvent viscosity was a crucial factor in controlling the stripping rate due to its high membrane thickness. Binary mixtures [Bmim+Emim][NTf_2] had the best stripping efficiency (84%) compared to the stripping efficiency of [Emim][NTf_2] (79%). The results indicated that a binary mixture of ionic liquids is a better choice as a membrane solvent than a single ionic liquid. Kogelnig et al. [119] examined the separation of iron(III) from hydrochloride solution with ionic liquid [P_{66614}][Cl] (or Cyphos IL101) in a BILM system. They reported that a BILM system with [P_{66614}][Cl] in chloroform (0.01 M) achieved a successful quantitative transport of 0.1 M iron(III) from a 6 M HCI solution (feed phase) to a 0.5 M HCI solution (receiving phase). Mirea et al. [121] evaluated the transport of iron (III) cations in HCl medium through BILM using Aliquat 336 as a carrier in chloroform. The efficiency was higher than 90% at the optimal transport conditions. Fe (III) cations form various chemical species of the type $FeCl_n^{3-n}$ (n = 1-4) in HCl medium and Aliquat 336 is used as a carrier for anionic species, the transport mechanism was shown in Figure 3(b).



(a)

(b)

Figure 3. Schematic representations of the transport of some chemical materials through BILM **(a)** Feed (F) phase: phenol in aqueous solution, Membrane (M) phase: [Bmim][NTf_2], Stripping (S) phase: NaOH, based on [66]. **(b)** Feed (F) phase: Fe (III) cations in HCl medium, Membrane (M) phase: Aliquat 336 in chloroform, Stripping (S) phase: HCl, based on [121].

Table 2. Summary of BLM and BILM studies reported for the separation of various compounds from aqueous solution.

Target Substance	Feed	Liquid Membrane Type	Membrane Solvent	Carrier	Strip	Ref.
Phenolic compounds	p-nitrophenol	BLM	Toluene	-	NaOH	[122]
			Toluene, benzene, p-xylene			[123]
	Phenol	BILM	[Bmim][FAP], [Bmim][PF$_6$], and [Bmim][NTf$_2$]	-	NaOH	[66]
	Chlorophenol		[Bmim][BF$_4$], [Bmim][PF$_6$], and [Bmim][Cl]	-	NaOH	[116]
	Phenolic compounds		[Emim][NTf$_2$], [Bmim][NTf$_2$], [Bmim][PF$_6$], and [Hmim][PF$_6$]	-	NaOH	[117]
Amino acids	l-phenylalanine, l-tryptophan, l-leucine, and l-isoleucine	BLM	Kerosene	D2EHPA	HCl	[124,125]
	Trp-OMe, Phe-OMe, Tyr-OMe and Trp		Chloroform	Calix[6] arene hexacarboxylic acid	H_2SO_4	[126]
	l-phenylalanine, l-phenylglycine, and l-tryptophan	BILM	[Omim][PF$_6$]	-	water	[118]
Heavy metals	Copper	BLM	Kerosene	LIX 984N, CYANEX 272, D2EHPA	H_2SO_4	[127]
	Lead, zinc, nickel, iron (II) and iron (III)		Chloroform	8-hydroxyquinoline (oxine), 2-amino pyridine, citric acid and glycine	EDTA, EGTA, HCl and HNO_3	[128]
	Iron (III)	BILM	Chloroform	[P$_{66614}$][Cl]	HCl	[119]
			Chloroform	Aliquat 336	HCl	[121]
Non-metallic compounds	Iodine	BLM	Kerosene	-	NaOH Na_2SO_3	[42]
Lignin compounds	Lignosulfonate	BLM	Heptane, hexane, carbon tetrachloride, chloroform, toluene and dichloroethane	TOA	NaOH NaCl Na_2CO_3	[129]
Drugs	5-aminosalicylic acid (mesalazine)	BILM	Chloroform	Aliquat 336	HCl	[130]
	Acetaminophen		Carbon tetrachloride and heptane		NaCl	[131]
	Ibuprofen, diclofenac, carbamazepine, and sulfamethoxazol	BLM	Dihexyl ether, decane, undecane and decanol	TOA, octane sulfonic acid and Cu(II)-chelate compound	Na_2CO_3, NaOH, HCl, and $HClO_4$	[132]
Antibiotics	Cephalexin	BILM	Butyl acetate	Aliquat 336	Buffer solution	[133]
	7-aminocephalosporanic acid					[134]
Carboxylic acids	Formic, acetic, propionic, and butyric acids	BLM	Oleyl alcohol	TBA	Water and NaOH	[135]
	Acetic and propionic acids		Toluene	TOA	NaOH	[136]
	Butyric acid		N-alkanes	TOA	NaOH	[137]
	5-methyl-2-pyrazinecarboxylic Acid		Xylene	TOA	NaOH	[138]
	Benzoic acid		Isooctane and dodecane	-	water	[139]
	Formic, acetic, acrylic and levulinic acids	BILM	[Bmim][TF$_2$N], [Bmim][PF$_6$], [Hmim][TF$_2$N], [Hmim][PF$_6$]	TBP	Water and NaOH	[6,11,40,45]
	Nicotinic acid		[Bmim][PF$_6$]			[120]
Dyes	Methylene blue	BLM	Chloroform, hexane, methylene chloride, carbon tetrachloride	CYANEX 301	H_2SO_4	[140]
			Benzene	Salicylic acid	Oxalic acid	[141]
			Chloroform or dichloromethane	P[5]-iodine	Water	[142]
Artificial sweeteners	Aspartame	BILM	Chloroform	Aliquat 336	HCl	[143]

3.2. Supported liquid membranes

Supported liquid membranes (SLMs) represent liquid membrane processes consisting of an organic liquid membrane phase immobilized into the pores of a microporous polymeric membrane or an inorganic film as support. It is placed between aqueous feed and stripping phases. The organic liquid membrane can contain a carrier or complexing agent for the highly selective separation of the target material from the feed phase [144–146]. The membrane support acts as a support matrix for the organic liquid phase [147]. Common membrane support configurations are available like hollow fibers, flat sheet, spiral, tubular, plate-and-frame modules [39].

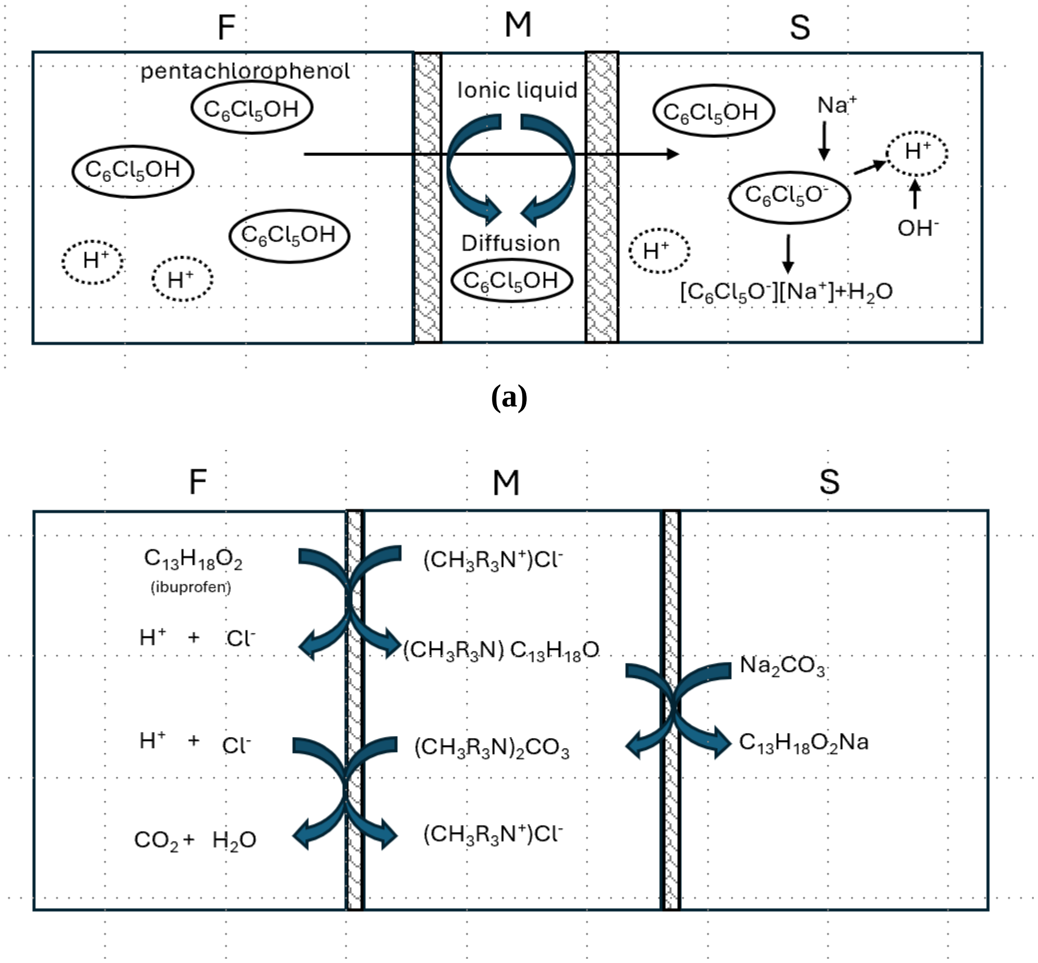
In an SLM process, the target material can be transported from the feed phase to the supported membrane, and then passes through the support membrane to reach the strip phase. The transport across the membrane phase is driven by the concentration gradient of the target material across the membrane, resulting in permeate dissolution in the membrane and diffusion across the membrane phase. Extraction continues as long as the concentration gradient exists and SLM operates without equilibrium limitation [39].

The SLM process has many advantages: ease of scaling up, high selectivity and permeability, energy saving, low operating and capital costs and the small amount of membrane phase needed [39,148]. The most important disadvantage of SLM is the lack of long-term stability of the membrane owing to some parameters, such as solubility of components from the membrane phase into the aqueous phases, emulsion formation at the membrane-aqueous interface, osmotic pressure difference over the membrane (*i.e.* between feed and strip) which removes the organic solvent and/or carrier from the micropores of the support. The loss of organic phase to the aqueous feed and strip phases may eventually lead to mixing of feed and stripping solutions and may also cause the failure of the separation. Attempts have been made by researchers to overcome this disadvantage by stabilizing the SLM [39,148–150]. It has been reported that the loss of membrane phase can be reduced by the selection of an appropriate membrane composition [148]. Kemperman et al. [151] reported that osmotic pressure may have an impact on the SLM instability if the membrane phase has sufficient water content. In case the membrane phase can dissolve a notable amount of water, an osmotic pressure difference may occur, and water transport is observed, which may have an impact on the instability of SLMs. To maximize the stability of SLMs, SLM systems should be designed with a low water solubility of the membrane phase, a low tendency of the support to be wetted by aqueous phases, and high organic/water interfacial tensions. Considering membrane phase components such as organic solvent, carrier (or additive) and the support, it is clear that the organic solvent has a great impact on SLM stability. However, the support characteristic affects SLM stability. In general, supports with a lower pore size are more stable. Another important support feature is the wettability of the membrane. The absorption of aqueous phases into the SLM is minimized if the support is sufficiently wetted by the organic solvent. Apart from these, SLM stability may be affected membrane thickness, carrier concentration, aqueous solute concentration, and operating conditions (e.g. high temperature, stirring rate or pumping velocity) [151].

To overcome the disadvantages of SLMs, ionic liquids can be used instead of conventional organic solvents [148,150,152]. The simplest approach to using ionic liquids as separation membranes is via SLM, in which the ionic liquid is immobilized into the pores of an inert porous support. Membranes containing an immobilized ionic liquid are called supported ionic liquid membranes (SILMs) [98]. Their stability is mainly affected by the features of the support membrane, such as type, porosity or pore size or porosity, the properties of IL such as hydrophobicity, viscosity, or surface tension and compatibility between IL and support membrane. Generally, membranes with a pore size are more appropriate for the preparation of SILMs between 100-200 nm. A high porosity of support membrane is preferred because it can support the ionic liquid under hydrostatic pressure. Also, transport efficiency can be increased by providing more surface area. For the viscosity of ILs, ILs with high viscosity cannot be easily removed from the pores of the support membrane, while ILs with low viscosity are prone to be displaced from the pores of the support. Based on a hydrophobic IL, SILMs prepared with hydrophobic membrane support are more stable than those prepared with hydrophilic support membrane due to the possible weak interaction between the hydrophilic support membrane and the hydrophobic IL [5]. To summarize, the correct selection of ILs can considerably improve the SILMs stability. As shown in Table 3, SILMs instead of SLMs have been used lately for the separation of various chemical compounds in aqueous medium, such as heavy metals [55,153,154], rare earth metals [103,155], carboxylic acids [145,156], phenols [39,157], drugs [147], hydrocarbons [158], and SILM can also be used in the separation of gas mixtures [98,159]. Asadollahzadeh et al. [103] investigated the extraction of rare earth metals (praseodymium and neodymium ions) from NdFeB magnet-leaching solution using SLM and SILM with TOPO and TBP in kerosene or ionic liquid [Hmim][NTf_2]. They obtained the highest permeability of a SILM with the synergistic system containing [Hmim][NTf_2], TOPO, and TBP. They also found that the SILM system was more stable with ionic liquid [Hmim][NTf_2]. Nosrati et al. [39] evaluated the performance of different ionic liquids ([Bmim][PF_6], [Bmim][NTf_2], [Bmim][BF_4], [Hmim][PF_6], [Hmim][BF_4], [Emim][HSO_4], [Bmim][HSO_4], [Bmim][FAP], [P_{66614}][NTf_2], and TOMAC) in SILM for the removal of phenol from wastewater. They achieved 85% phenol removal by using a minimal loss amount of [Bmim][HSO_4] with PTFE membrane support. This SILM system remained stable for more than 24 hours. They attributed the more stable liquid membrane containing [Bmim][HSO_4] to its higher viscosity. They also reported that the SILM system with TOMAC occurs to a reaction between TOMAC and the feed solution. Ionic liquids consisting [HSO_4] anion indicated a higher SILM stability and performance. [Hmim][BF_4] also had a better removal than [Bmim][BF_4]. They revealed this result that enlarging the alkyl chain length in the cation can enhance the ionic liquid performance. Fan et al. [61] recommended that the hydrophobic effect of the imidazolium cation and the hydrogen bond of the anion play an important role on the removal performance.

Panigrahi et al. [146] investigated the removal of endocrine disrupting chemical (Bisphenol A) from aqueous solution using SILM. They used PVDF membrane as a support, and ionic liquids based on different cations such as imidazolium, phosphonium, pyridinium, and ammonium. The maximum permeation of 62% was obtained for ionic liquid [TBP][PF_6]. Aliquat 336 and ammonium based ionic liquids did not gave good permeation rate compared to imidazolium and phosphonium based ionic liquids. The permeation rate also ordered as [TBP][PF_6] > [Omim][PF_6] > [EDmim][PF_6] > [P_{66614}][Br] > [BTNH][BTA] > [TBTDP][BTMPP] > [P_{66614}][Cl] > Aliquat 336> [BMPYR][BTA]. These ionic liquids showed good a SILM stability over 24 h with a maximum. They also reported that membrane weight loss of 2%. They also reported that less viscous ionic liquids had a greater membrane weight loss. Fortunato et al. [118] investigated the liquid-liquid extraction of amino acid esters (proline benzyl ester, phenylglycine methyl ester, and phenylalanine methyl ester) and amino acids (phenylglycine, phenylalanine, and tryptophan) using ionic liquid [Omim][PF_6]. They reported that [Omim][PF_6] had a good selectivity for the amino acid esters tested but a negligible selectivity for amino acids. Later, they tested the transport of amino acid esters and amino acids through a SILM with [Omim][PF_6] and a loss of selectivity was observed, and so amino acid esters and amino acids were transported at similar rates. They concluded that the transport at first was mainly executed by ionic liquid selectivity toward each compound, and then water microenvironments occur and hence the transport through these microenvironments becomes the dominant mechanism. Schematic representations of the transport of some chemical materials through SILM are given in Figure 4. As reported in the literature [157,160], generally, H-bonding and hydrophobic interactions between ionic liquid and phenolic compounds play a significant role in transport of phenolic compounds from aqueous medium into an ionic liquid membrane. Pilli et al. [157] investigated the separation of pentachlorophenol from water by a SILM consisting of ionic liquids [BDmim][PF_6] and [TBP][PF_6] immobilized on a PVDF membrane. They reported that the transport mechanism of pentachlorophenol via SILM could be explained by H-bonding and hydrophobic interactions between cation of ionic liquid and aromatic ring of phenolic compound. Harun et al. [147]studied the transport mechanism of ibuprofen through SILM containing ionic liquid Aliquat 336, as shown in Figure 4(b). Aliquat 336 consists of quaternary ammonium salt and chloride [$C_nH_nN^+Cl^-$]. A reaction takes place at the feed side of the SILM between undissociated ibuprofen and ionic liquid Aliquat 336 and forms soluble extractable complexes. The complexes are transported through the SILM to the stripping side of SILM and the reaction takes place between the complexes and Na_2CO_3 forming amine carbonate and sodium ibuprofen. Then, the amine carbonate diffuses back into liquid carrier and the carrier is regenerated, releasing gaseous CO_2.

From these studies and their results, it is clear that SILMs show a longer stability performance and a higher flux and selectivity. Moreover, the characteristic performance of each ionic liquid points out that the ionic liquid selection is substantial. SILM is a relatively novel technology that is not extensively utilized, but it has a high potential for the removal of various species from aqueous environments.



(a)

(b)

Figure 4. Schematic representations of the transport of some chemical materials through SILM **(a)** Feed (F) phase: pentachlorophenol in aqueous solution, Membrane (M) phase: [BDmim][PF_6] or [TBP][PF_6] immobilized on PVDF support, Stripping (S) phase: NaOH, based on [157]. **(b)** Feed (F) phase: ibuprofen in aqueous solution, Membrane (M) phase: Aliquat 336 in a solvent (kerosene, hexane, sunflower oil, palm oil or rice bran oil) impregnated on PVDF support, Stripping (S) phase: Na_2CO_3, based on [147].

Table 3. Summary of SLM and SILM studies reported for the separation of various substances from aqueous solutions.

Target Substance	Feed	Liquid Membrane Type	Membrane	Strip	Ref.
Phenols	Phenol in aqueous solution	SLM	TOPO in 2-nitrophenyl octyl ether, decane, 2-octanol and kerosene, PP and PVDF as flat-sheet polymeric supports	NaOH	[161]
		SILM	[Bmim][PF$_6$], [Bmim][NTf$_2$], [Bmim][BF$_4$], [Hmim][PF$_6$], [Hmim][BF$_4$], [Emim][HSO$_4$], [Bmim][HSO$_4$], [Bmim][FAP], [P$_{66614}$][NTf$_2$], TOMAC, PVDF and PTFE membranes as polymeric supports		[39]
	Pentachlorophenol in aqueous solution		[BDmim][PF$_6$] and [TBP][PF$_6$], PVDF membrane as the support		[157]
Drugs	Diclofenac in aqueous solution	SLM	CYANEX 923 in kerosene, PTFE as polymeric supports	Water	[162]
	Diclofenac and ibuprofen in aqueous solution		CYANEX 923 in kerosene, a hollow fiber module membrane consisting of polypropylene /polyethylene material	Water	[163]
	Ibuprofen in aqueous solution	SILM	Aliquat 336 in kerosene, hexane, sunflower oil, palm oil, and rice bran oil, PVDF as support	Na_2CO_3	[147]
Heavy metals	Cr (VI) in aqueous solution	SILM	Aliquat 336 in kerosene, PET membrane as a porous support	HCl	[153]
	Hg(II), Cd(II) and Cr(III) in aqueous solution		[iOMim][D2EHP] in dodecane, PVDF membranes as supports	HNO_3	[55]
Lithium	LiCl LiCl + NaCl LiCl+$MgCl_2$ Li_2SO_4+$CoSO_4$ +$NiSO_4$	SILM	TBP in [Emim][NTf$_2$], [Bmim][NTf$_2$], [Hmim][NTf$_2$], [Omim][NTf$_2$], [N$_{1114}$][NTf$_2$], [P$_{66614}$][NTf$_2$], PVDF membranes as polymeric supports	Na_2CO_3/$NaHCO_3$	[144]
Rare earth metals	Rare earth elements from acid mine drainage	SLM	A mixture of 10% v/v DEHPA and 90% kerosene, PVDF membrane as a support	HNO_3	[164]
	Neodymium and praseodymium ions from leaching solution		TOPO and TBP in kerosene	HNO_3, HCl, and H_2SO_4	[103]
		SILM	TOPO and TBP in [HMIM][NTf$_2$]		
	Lanthanum in $NaNO_3$ solution		TBP in [Bmim][Tf$_2$N], PVDF membrane as a support	Water	[155]
Carboxylic acids	Levulinic acid in aqueous solution	SILM	Aliquat 336, TOPO, TOA, or TDA in 2-ethyl-1-hexanol, Hybrid graphene- polyethersulfone flat sheet membrane	NaOH	[145]
	Glutamic acid in aqueous solution				[156]
Hydrocarbons	Benzene, toluene and p-xylene mixture	SILM	[Bmim][PF$_6$], [Hmim][PF$_6$], [Omim][PF$_6$], [Et$_2$MeMeON][NTf$_2$], PVDF membrane as a support	Hexadecane	[158]
Dyes	Rhodamine B and Methylene blue in aqueous solution	SLM	Mixtures of M2EHPA, D2EHPA and nanoparticles were used as carrier in Sesame oil, PTFE membrane as a support	Acetic acid	[165]
	Rhodamine B		Xylene as a carrier in phenol, PTFE membrane as a support		[166]
Endocrine disrupting chemicals	Bisphenol A in aqueous solution	SILM	[P$_{66614}$][Cl] , [P$_{66614}$][Br], [TBP][PF$_6$] [TBTDP][BTMPP], Aliquat 336, [Omim][PF$_6$],[BTNH][BTA], [EDmim][PF$_6$], [BMPYR][BTA] PVDF membrane as a support	HCl	[146]

3.3. Emulsion liquid membranes

Emulsion liquid membranes (ELM) consist of three phases: an external phase (feed phase), an organic phase (membrane phase), and an internal phase (stripping phase). The organic liquid membrane phase comprises diluents, carriers, and/or surfactants. The external phase is a liquid phase carrying the target solute to be separated, while the internal phase is the liquid phase that captures the separated solutes [167]. ELM has also a variety of benefits including the single-step extraction and stripping stages, high selectivity, high speed of water treatment, environmental compatibility, easy control, ease of reduction, and manufacturing of double phase final product [168]. The only drawback of ELM is the instability of the emulsion. The stability of the emulsion is a significant criterion determining the potential of an ELM [169]. In this context, the selection of a solvent or diluent is a substantial factor that contributes to the stability of the emulsion. Many studies have indicated that the membrane stability is based on the composition of the membrane [41,78,170]. For a good membrane stability, an external agent, an extractant or carrier, is needed [169].

As a separation technique, organic solvents such as petroleum-based diluents including kerosene, n-heptane have extensively been utilized in ELM. As mentioned before, these types of organic solvents, which are toxic, highly flammable, and volatile, cause water contamination, environmental problems, and process-related risks. Hence, it is preferable to replace these solvents with green solvents that have non-toxic properties and have less impact on the environment. In this regard, ionic liquids [169,171], or non-toxic edible vegetable oils [167,172] are recommended as environmental and green solvents in ELM processes.

ELM is widely used for the investigation of the separation of heavy metals [173–175], phenols [167,176–178], and dyes [172,179–182]. In recent years, EILM was found to have a high potential to be used instead of ELM, which is used for the separation of various chemical species in aqueous medium, such as heavy metals [168,183], carboxylic acids [184], phenols

[65,171,185], drugs[169,186], pesticides [187], and dyes [78]. Mesli and Belkhouche [183] evaluated the recovery of Pb(II) from nitrate aqueous solution by the ionic liquid Aliquat 336 as a carrier and Tween20 as a surfactant using EILM technique. They obtained that Pb(II) ions were extracted at 82.61% in an ionic liquid membrane, and pre-concentrated at 82.16% in nitric acid solution at the optimal experimental conditions ([Aliquat 336] = 1% w/w; [Tween20] = 0.5% w/w; [Pb(II)] = 207.2 ppm; pH of feed phase: 5.5; extraction time: 30 min; and stirring speed: 210 rpm). They were also tested Pb(II) and Cu(II) separation under the optimal conditions of Pb(II) recovery. It was concluded that Pb(II) was extracted and pre-concentrated more than Cu(II). Harun and Ahmad [186] investigated ibuprofen removal from aqueous solution through an EILM technique consisted of the ionic liquid Aliquat 336 as a carrier, Span 80 as a surfactant, and Na_2CO_3 as a strip phase. The highest ibuprofen extraction (96.78%) was obtained at the optimum conditions of Aliquat 336 concentration of 2 wt%, Span 80 concentration of 4 wt% and Na_2CO_3 concentration of 0.1 M. Khan et al. [169] performed a screening of ionic liquid combinations using COSMO-RS for ibuprofen extraction. The best suitable ionic liquid was used for developing EILM technique for the removal of ibuprofen. COSMO-RS results suggested that the combinations of quaternary ammonium cations consisting of Cl^- and SO_4^{2-} anions gave the best extraction ability, as these anions have a better bonding ability and higher electronegativity. Non-coordinating anions like BF_4^- and PF_6^- anions have weak bonding abilities, and they were not appropriate for ibuprofen removal. The selected ionic liquids [TMAm][SO_4], [TMAm][Ac], [TMAm][Cl], [Bmim][Cl], [BMPyrro][Cl], [BMPyrro][Br], and [Ch][Cl] were studied in EILMs for the experimental verification of COSMO-RS. Span 80 as a surfactant, sunflower oil as a diluent, and NaOH as a stripping phase were used in these EILM systems. These developed EILMs were highly stable and efficient for the removal of ibuprofen. An EILM consisting of ionic liquid [TMAm][SO_4] was found to be the best with ionic liquid [TMAm][SO_4] concentration of 0.25 wt.%, the breakage of 1.2%, and the maximum extraction efficiency of 93.5%. A new EILM combination of ionic liquid [Bmim][PF_6] dissolved in TBP was examined for the separation of phenolic compounds such as phenol, p-chlorophenol, pentachlorophenol, 2,4 dichlorophenol, and 2,4,6 trichlorophenol from a synthetic aqueous solution by Balasubramanian and Venkatesan [178]. They found that the addition of 0.02% (v/v) of [Bmim][PF_6] in membrane phase increased the emulsion stability by a factor 5. The maximum removal of 99.5% for phenol and 90% for chlorophenols was obtained at optimal experimental conditions, i.e., TBP concentration: 0.2%; Span 80 concentration: 4% (v/v); NaOH concentration in strip phase: 0.25 N; feed phase pH: 6.5; phase volume ratio (I/M): 1; emulsification time: 5 min; emulsification speed: 8000 rpm; and agitation speed: 200 rpm. The selectivity followed as phenol> p-chlorophenol > 2,4-dichlorophenol > 2,4,6-trichlorophenol > pentachlorophenol. Venkatesan and Meera Sheriffa Begum [187] investigated the separation of benzimidazole (a pesticide and fungicide) from aqueous solutions by EILM using an ionic liquid TOMAC. They found that TOMAC is an appropriate carrier for benzimidazole separation in ELM system. EILM optimum conditions were determined as surfactant Span 80 concentration of 4% (v/v), emulsification speed of 10000 rpm, emulsification time of 6 min, TOMAC concentration of 0.5% (v/v), HCl concentration in internal phase of 0.3 M, internal phase pH of 6, external pH of 13, stirring speed of 200 rpm, volume ratio of organic phase to internal phase (O/A):1, and volume ratio of external to emulsion of 1. The emulsion was stable up to 140 min. The percentage extraction of benzimidazole was 97.5%. Thakur et al. [78] examined the recovery of anionic dye Procion blue MX-R dye from an aqueous solution using nanoparticle-ionic liquid-based emulsion liquid membrane. EILM was comprised of [Bmim][Cl] in rice bran as the diluent, Aliquat 336 as a carrier, Span 80 as the surfactant incorporating ZnO nanoparticles and NaOH in the internal phase. The recovery efficiency for Procion blue MX-R dye was 98.71 ± 0.95% at the optimum conditions, including dye concentration of 45 ppm, Aliquat 336 concentration of 0.9% (v/v), ZnO nanoparticle concentration 0.06% (w/v), NaOH concentration of 0.095 N, contact time of 12 min, and agitation speed of 498.6 rpm. They also explained the detailed mechanism of Procion blue MX-R dye recovery with the aid of Aliquat 336 based EILM. As presented in Figure 5(a), the mechanism occurs of a two-step operation consisting interaction between Aliquat 336 and Procion MX-R dye species in the form of $[CH_3R_3N]^+[Cl]^-$ and $2[H]^+[C_{23}H_{12}Cl_2N_6O_8S_2]^-$, respectively. Khan et al. [188] developed a novel EILM for the removal of lactic acid from aqueous solution consisting of olive oil as the diluent, three different ionic liquids ([TMAm][Cl], [TMAm][Ac] and [TBMAm][Cl]) as the carriers, NaOH as stripping solution, Tween 80 and Span 20 as emulsifier. They achieved a maximum lactic acid removal efficiency of 94.5% for an ionic liquid [TMAm][Ac] under the optimized conditions of lactic acid concentration of 0.05 M, Span 20 concentration of 1.0 wt.%, NaOH concentration of 0.3 M, [TMAm][Ac] concentration of 0.3 wt.%, the ratio of internal phase to diluent phase of 0.3 and the ratio of external phase to membrane phase of 3:1. They also clarified the mechanism for lactic acid removal through EILM involved ionic liquid [TMAm][Cl] as a carrier. The removal of lactic acid takes place with formation of ionic liquid-acid complexes resulting in H-bonding interactions between ionic liquid and acid. Due to the presence of water-soluble anion in ionic liquid [TMAm][Cl], an ion exchange mechanism is expected to occur at the membrane-stripping interface. Thus, Cl^- is replaced by OH^- and another carrier $[TMAm^+OH^-]$ is formed. Eventually, the EILM system contains two carriers $[TMAm^+Cl^-]$ and $[TMAm^+OH^-]$ for the removal of lactic acid and two ionic liquid- lactic acid complexes $[TMAm^+Cl^- - C_3H_6O_3]$ and $[TMAm^+OH^- - C_3H_6O_3]$ forms at the feed-membrane interface. These complexes diffuse through the membrane phase and reach to the stripping phase (internal phase). They react with NaOH in the stripping phase to convert into the sodium form of lactic acid and the carrier is regenerated for further use. The detailed removal mechanism for lactic acid with ionic liquid [TMAm][Cl] through the EILM is also represented in Figure 5(b). The results obtained in the literature indicate that EILM methodology is feasible for separation of various compounds from aqueous mixtures. A summary of ELM and EILM studies reported is also given in Table 4.

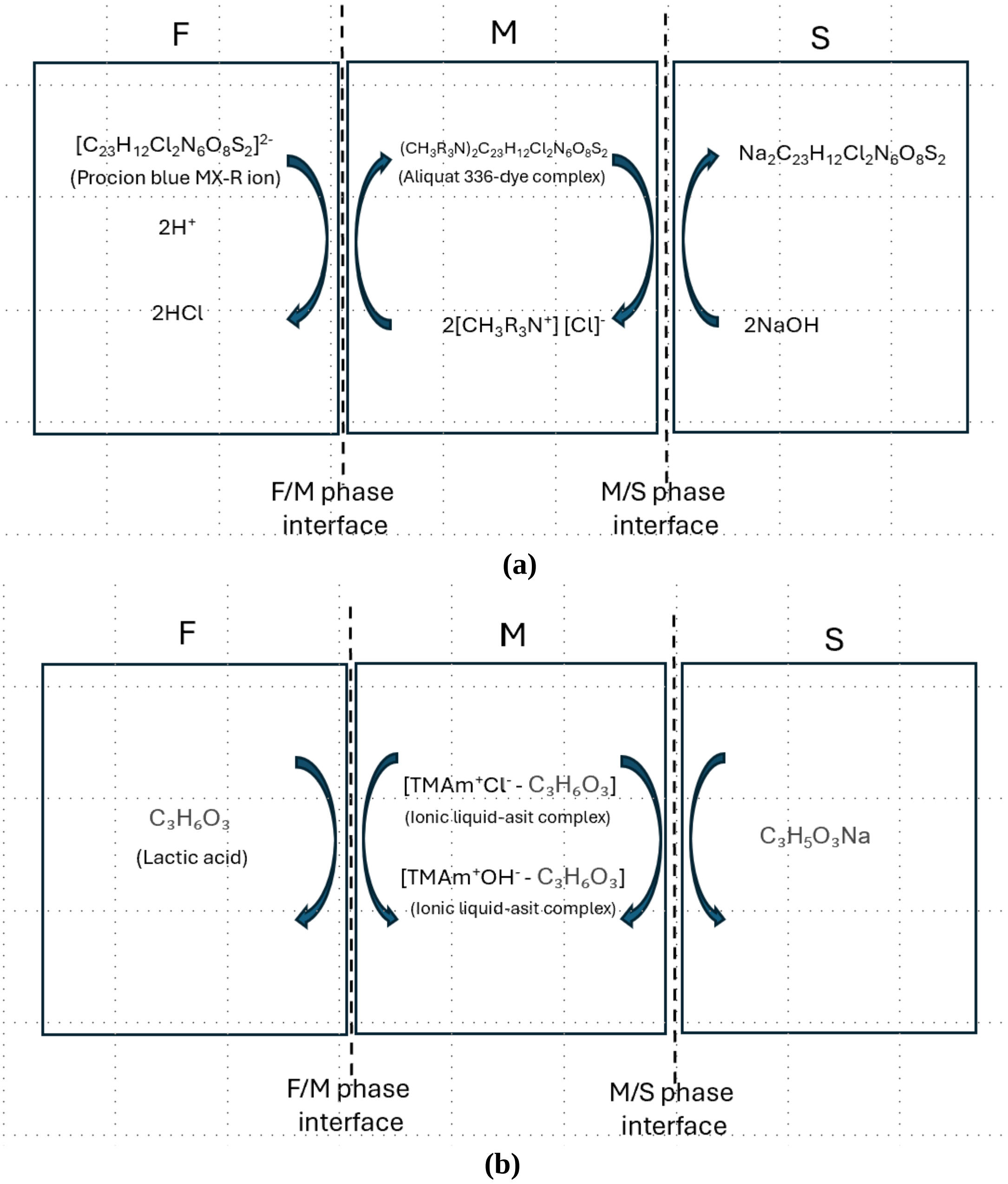


Figure 5. Schematic representations of the transport of some chemical materials through EILM **(a)** Feed (F) phase: Procion blue MX-R dye in aqueous solution, Membrane (M) phase: [Bmim][Cl] in rice bran, Aliquat 336, Span 80, and ZnO nanoparticles, Stripping (S) phase: NaOH, based on [78]. **(b)** Feed (F) phase: lactic acid in aqueous solution, Membrane (M) phase: olive oil, [TMAm][Cl], and Span 20, Stripping (S) phase: NaOH, based on [188].

Table 4. Summary of ELM and EILM studies reported for the separation of various substances from its aqueous solutions in literature.

Target Substance	Feed	Liquid Membrane Type	Membrane	Strip	Ref.
Phenolic compounds	Phenol in aqueous solutions	ELM	Palm oil as the diluent, Span 80 as the surfactant	NaOH	[167]
		EILM	[Bmim][NTf$_2$] as a stabilizer, a mixture of kerosene and palm oil as diluent, blended surfactant of Span 80 and Tween 80 as the surfactant	NaOH, HCl, H_2SO_4 and acidic thiourea solution	[171]
	Phenol, p-chlorophenol, 2,4 dichlorophenol, 2,4,6 trichlorophenol, pentachlorophenol in aqueous solution		[Bmim][PF$_6$] dissolved in TBP, kerosene as a diluent, Span 80 as a surfactant	NaOH	[65]
Heavy metals	Co(II) from aqueous thiocyanate medium	ELM	CYANEX 923 as the extractant in cyclohexane, SPAN 80 as the surfactant	H_2SO_4	[173]
	Pb(II) in aqueous solution	EILM	Aliquat 336 as an ionic liquid carrier, edible paraffin as a solvent, Tween 80 as a dispersive non-ionic surfactant	NaOH	[168]
Drug	Naproxen in phosphate buffer solution	ELM	Soybean oil as the solvent and carrier, a mixture of Abil EM 90®; 0.15wt% – 0.5wt% as the surfactant	$NaHCO_3$	[189]
	Ibuprofen in aqueous solution	EILM	Quaternary ammonium-based ILs as the extractant, sunflower oil as the diluent, Span 80 as the surfactant	NaOH	[169]
			Aliquat 336, Span 80 as the surfactant	Na_2CO_3	[186]
Carboxylic acids	Lactic acid in aqueous solution	EILM	Aliquat 336, and TDA as extractants, rice brain oil as a solvent, hexane as a diluent, Span 80 as a surfactant	NaOH	[184]
			Olive oil as the diluent, [TMAm][Cl], [TMAm][Ac] and [TBMAm][Cl] as the carriers, Tween 80 and Span 20 as the surfactants	NaOH	[188]
Dyes	Methyl violet 2B in aqueous solution	ELM	Sunflower oil as the diluent, Span 80 as the surfactant	HCl	[172]
	Acid orange 7 in aqueous solution		Heptane, kerosene, and cyclooctane as the diluent, TDA as the extractant, Span 80 as the surfactant	H_2SO_4	[190]
	Procion Blue MX-R in aqueous solution	EILM	[Bmim][Cl] in rice bran oil as the diluent, Aliquat 336 as the carrier, Span 80 as the surfactant incorporating ZnO nanoparticles	NaOH	[78]
Pesticides	Alpha-cypermethrin pesticide in aqueous solution	ELM	Sunflower oil and kerosene as the diluents, Span 80 and Tween 80 the surfactants	NaOH	[191]
	Benzimidazole in aqueous solution	EILM	TOMAC as an extractant in n-heptane–kerosene mixture, Span 80 as the surfactant	HCl	[187]

4. Conclusion and future trends

The demand for highly efficient, rapid, cost-effective, and environmentally friendly separation and purification processes has led to significant efforts in the development of new techniques. Despite the economic benefits, the application of conventional organic solvents in separation processes brings with it certain challenges arising from their toxic and denaturing nature. ILs are a suitable alternative to conventional organic solvents due to their superior features and eco-friendliness. The combination of liquid membrane technology with ILs appears to be a promising separation technique that can be used in various applications. In this review, IL-based liquid membrane (ILM) technology, targeting different kinds of ILMs, i.e., bulk ionic liquid membranes (BILMs), supported ionic liquid membranes (SILMs) and emulsion ionic liquid membranes (EILMs), used in the separation of various chemical species from aqueous media is summarized. Especially, the separation of target substances from aqueous solutions through ILMs was examined in this study. When the studies in the literature were examined, ionic liquid membranes have been used for the separation of various chemical compounds in aqueous medium, such as phenols, drugs, amino acids, dyes, hydrocarbons, metals, carboxylic acids, pesticides and gas mixtures. They resulted in very high removal efficiencies (up to 99.5%) from aqueous solutions. They also indicated that the H-bonding and hydrophobic interactions between ionic liquid and target compounds play a significant role in separation of chemical compounds from aqueous medium into ionic liquid membranes. These results present beneficial sources to develop novel ILMs for specific target substances. Thanks to the combined advantages of ionic liquids and liquid membranes, such as selectivity, stability, applicability, and versatile functions, ILMs have become a promising research area with a wide variety of potential separation applications. Moreover, the compatibility between membrane and ionic liquids and stability of ILMs were discussed. The major challenge of liquid membranes is their lack of long-term stability. To overcome this challenge, it is significant to design new ILMs that have long-term stability and compatibility between the IL and support membrane in specific applications. Compared to the LMs, ILMs are more stable due to the properties of ionic liquids. Understanding the functions and structures of ionic liquids can facilitate the design of new ILM technologies. This review will also contribute to the choice of ionic liquids to obtain higher removal efficiencies and stable ILMs. Although ILMs allow for notable progress for the separation of target substances from aqueous medium, there are important challenges needed to be addressed and solved. The interaction mechanism between the other target materials and ionic liquids needs to be further explained. There is still a gap in the fundamental knowledge needed to develop and optimize separation procedures, especially when it comes to other different ILs. Also, there is still a great need for developing ILM methodologies for the separation of other components from aqueous media or wastewater. In this context, it is recommended to investigate the separation of other target materials from aqueous solutions or different areas that have not been studied by ILMs. It needs to be revealed that these target materials can separate in real environments with ILMs technologies that provide a stable performance over long periods of time. Furthermore, the long-term performance and economic analysis of ILMs needs to be studied for large-scale industrial applications.

Declaration of Competing Interest

The authors declare no competing interests.

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CRediT authorship contribution statement

Nilay Baylan: Conceptualization, Investigation, Visualization, Writing – original draft.

Gilles Van Eygen: Conceptualization, Investigation, Writing – review & editing.

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Symbols:

[Emim][Ac]	1-butyl-3-methylimidazolium acetate
[Emim][DCA]	1-Ethyl-3-methylimidazolium dicyanamide
[Emim][NTf$_2$]	1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[Emim][BF$_4$]	1-Ethyl-3-methylimidazolium tetrafluoroborate
[Emim][SCN]	1-Ethyl-3-methylimidazolium thiocyanate
[Emim][TCM]	1-Ethyl-3-methylimidazolium tricyanomethanide
[Emim][HSO$_4$]	1-Ethyl-3-methylimidazolium hydrogensulfate
[Emim][CF$_3$SO$_3$]	1-Ethyl-3-methylimidazolium trifluoromethanesulfone
[Emim]$_2$[Co(SCN)$_4$]	Bis(1-ethyl-3-methylimidazolium) tetrathiocyanatocobaltate
[Bmim][DCA]	1-Butyl-3-methylimidazolium dicyanamide
[Bmim][NTf$_2$]	1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[Bmim][PF$_6$]	1-Butyl-3-methylimidazolium hexafluorophosphate
[Bmim][TCM]	1-Butyl-3-methylimidazolium tricyanomethanide
[Bmim][HSO$_4$]	1-Butyl-3-methylimidazolium hydrogensulfate
[Bmim][FAP]	1-Butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate
[Bmim][BETI]	1-Butyl-3-methylimidazolium bis(perfluoroethyl(suflonyl))imide
[Bmim][SCN]	1-Butyl-3-methylimidazolium thiocyanate
[Bmim][Cl]	1-Butyl-3-methylimidazolium chloride
[Bmim]$_2$[Co(SCN)$_4$]	Bis(1- butyl-3-methylimidazolium) tetrathiocyanatocobaltate
[Hmim][NTf$_2$]	1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[Hmim][PF$_6$]	1-Hexyl-3-methylimidazolium hexafluorophosphate
[Hmim][BF$_4$]	1-Hexyl-3-methylimidazolium tetrafluoroborate
[Hmim][Ac]	1-Hexyl-3-methylimidazolium acetate
[Omim][NTf$_2$]	1-Octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[Omim][PF$_6$]	1-Octyl-3-methylimidazolium hexaflourophosphate
[Omim][BF$_4$]	1-Octyl-3-methylimidazolium tetrafluoroborate
[Omim][Ac]	1-Octyl-3-methylimidazolium acetate
[Dmim][Ac]	1-Decyl-3-methylimidazolium acetate
[N$_{1114}$][NTf$_2$]	Trimethyl(butyl)ammonium bis(trifluoromethylsulfony)limide
[N$_{1888}$][SCN]	Tricaprylmethylammonium thiocyanate
[N$_{1888}$][DCA]	Tricaprylmethylammonium dicyanoamide
[N$_{1888}$][BA]	Tricaprylmethylammonium benzoate
[N$_{1888}$][Hex]	Tricaprylmethylammonium hexanoate
[P$_{66614}$][NO$_3$]	Trihexyl(tetradecyl)phosphonium nitrate
[P$_{66614}$][Cl]	Trihexyltetradecylphosponium chloride
[P$_{66614}$][Br]	Trihexyl(tetradecyl)phosponium bromide
[P$_{66614}$][DCA]	Trihexyltetradecylphosphonium dicyanamide
[P$_{66614}$][TCM]	Trihexyltetradecylphosphonium tricyanomethanide

[P$_{66614}$][C$_9$H$_{19}$COO]	Trihexyltetradecylphosphonium decanoate
[P$_{66614}$][(i-C$_8$)POO]	Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate
[E4mpy][NTf$_2$]	1-Ethyl-4-methylpyridinium bis(trifluromethylsulfonyl)imide
[B4mpy][TCM]	1-Butyl-4-methylpyridinium tricyanomethanide
[B4mpy] [NTf$_2$]	1-Butyl-4-methylpyridinium bis(trifluromethylsulfonyl)imide
[Bmpy][NTf$_2$]	1-Butyl-1-methylpyrrolidinium bis[(trifluoromethyl)sulfonyl]imide
[BMPyrro][Cl]	1-Butyl-1-methylpyrrolidinium chloride
[BMPyrro][Br]	1-Butyl-1-methylpyrrolidinium bromide
[BMMor]Cl	4-Butyl-4-methylmorpholinium chloride
[BMPip]Cl	1-Butyl-1-methylpiperidinium chloride
[DMIM][MP]	1,3-Dimethylimidazolium methylphosphite
[EDmim][PF$_6$]	1-Ethyl-2,3-dimethylimidazoliumhexaflourophosphate
[BDmim][PF$_6$]	1-Butyl-2,3-dimethyl imidazolium hexafluorophosphate
[Hmpy][NTf$_2$]	1-Hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide
[Ch][NTf$_2$]	Choline bis(trifluoromethylsulfonyl)imide
[Ch][Cl]	Choline chloride
[ABZIM]Cl	1-Allyl-3-benzylimidazolium chloride
[BZVIM][Cl	1-Benzyl-3-vinylimidazolium chloride
[DBZIM]Cl	1,3-Dibenzylimidazolium chloride
[C$_6$byp][NTf$_2$])	N-hexyl-4,4-bipyridiniumbis(trifluoromethylsulfonyl)imide
[HPhIm][NTf$_2$]	1-Hexyl-2-phenylimidazolium bis(trifluoromethanesulfonyl) imide
[BnMIm] [NTf$_2$]	1-Benzyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl) imide
[C$_n$C$_n$C$_n$C$_1$N][BTMPP]	Trialkylmethylammonium bis(2,2,4-trimethylpentyl)phosphinate
[TBTDP][BTMPP]	Tributyltetradecylphosponium bis(2,4,4-trimethylpentyl)phosphinate
[TBP][PF$_6$]	Tetrabutylphosphonium hexafluorophosphate
[TMAm][Ac]	Tetramethylammonium acetate
[TMAm][Cl]	Tetramethylammonium chloride
[TBMAm][Cl]	Tributylmethylammonium chloride
[TMAm][SO$_4$]	Tetramethylammonium sulphate
[BTNH][BTA]	1-Butyltrimethylammonium bis(trifluoromethylsulfonyl)amide
[BMPYR][BTA]	1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide
[Bvim][Br]	1-Butyl-3-vinylimidazolium bromide
[Et2MeMeON] [Tf$_2$N]	Diethylmethyl(2-methoxyethyl)ammonium bis(trifluoromethan sulfon) imido salt
[iOMim][D2EHP]	Isooctylmethylimidazolium bis-2-ethylhexylphosphate
[N333 MeOAc] [Tf$_2$N]	N,N,N-tripropyl-1-methyl acetate ammonium bistriflimide
[N444 MeOAc][Tf$_2$N]	N,N,N-tributyl-1-methyl acetate ammonium bistriflimide
Aliquat336	Methyltrioctylammonium chloride
M2EHPA	(2-etylhexyl) ester of phosphoric acid
D2EHPA	Di-2-ethylhexyl phosphoric acid
EDTA	Ethylenediaminetetraacetic acid

EGTA	Ethyleneglycoltetraacetic acid
TOMAC	Trioctylmethylammonium chloride
TOA	Trioctylamine
TBA	Tributylamine
TDA	Tridodecylamine
CYANEX 301	Bis(2,4,4-trimethyl pentyl)dithiophosphinic acid
CYANEX 272	Bis-2,2,4- trimethyl pentylphosphinic acid
CYPHOS IL-104	Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate
CYANEX 923	Mixture of straight chain alkylated phosphine oxides
LIX 984N	Mixture of 5-nonylsalicylaldoxime and 2-hydroxy5-nonylacetophenoneoxime
Trp-Ome	L,D-tryptophan methyl ester hydrochloride
Phe-Ome	L-phenylalanine methyl ester hydrochloride
Tyr-Ome	L-tyrosine methyl ester hydrochloride
Trp	L-tryptophan
PP	Polypropylene
PVDF	Polyvinyldene fluoride
PTFE	Polytetrafluoro ethylene