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Deep eutectic solvents – A new platform in membrane fabrication and membrane-assisted technologies

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Abstract

Deep eutectic solvents (DESs) are a new class of solvents that can offset some of the primary drawbacks of typical solvents and ionic liquids (ILs). Since DESs fall into the guidelines of “Twelve Principles of Green Chemistry”, their implementation in several types of applications has exponentially increased over the last years. The usage of DESs has been directed to the designing, manufacture and purification of new materials and feedstocks. Very recently, great attention has been paid to new pioneering attempts aiming at DESs into the field of chemical engineering, including membrane science and technology. Even if just a few works have been currently reported in applying DESs in membranes, the consideration on this new type of solvents is continuously growing. This review compares and discusses the documented discoveries and breakthroughs carried out in applying DESs in membrane science. The scope of this review is emphasized in various scopes: i) new sustainable membrane preparation, ii) membrane-based technologies aided by DESs, iii) target molecules-DES interactions and iv) new membrane-DES structures providing enhanced physicochemical properties and thus separation performance. Here, besides the relevant insights in the field, we give the key hypotheses and strategies used by the scientists to reach a successful merging of both areas since the use of DESs in membranes is still challenging due to the compatibility issues of the DESs and membrane phase (either polymer and inorganic). The future directions and perspectives on using DESs in membranes are also given.

Keywords: Green chemistry; deep eutectic solvents; membrane fabrication; membrane science and technology; separation techniques.

1. Introduction

Deep eutectic solvents (DESs) can be considered as a new class of solvents which have been recognized as ”green alternatives” to conventional solvents and ionic liquids (ILs) [1]. Their area of application is constantly growing and evolving, encompassing different applications including metal plating and coatings [2], sustainable media in organic reactions [3], extraction of biomolecules and chemical elements (Zn, Fe, Pb, etc.) from natural sources [4,5], analytical chemistry [6], removal of chemical contaminants from water and foods [7], CO_2 capture [8], desulfurization [9], formulation of stationary phases for chromatography [10], enzymatic biodiesel production [11], chemical catalysis [12], biotransformations [13], among others. Since the first introduction of choline chloride-based DES in 2003 by Abbott and co-workers [14], the implementation of DESs in modern chemistry has been exponentially explored as reflected in the growing number of publications on the topic (see **Figure 1**), demonstrating an increasing research interest in this field.

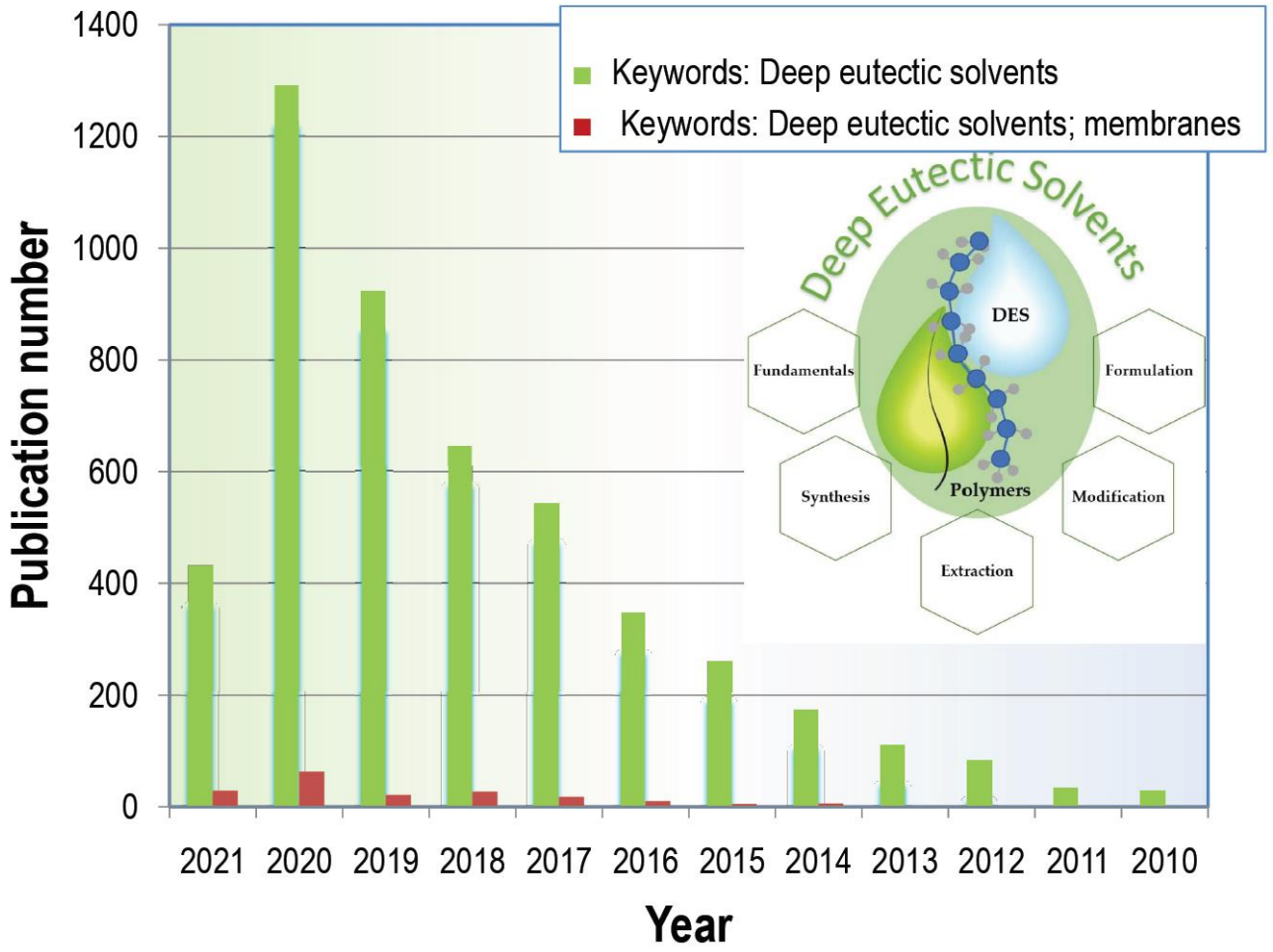

Figure 1. Publications related to the applications of DES over past 10 years (until April15th, 2021; source: Scopus). Studies in red are those related to the application of DESs in membranes.

Considering the "*Twelve Principles of Green Chemistry*" established by Anastas and Warner [15], DESs fully meet some of the proposed criteria (e.g. less hazardous synthesis, use of safer solvents and auxiliaries) fostering their use in various areas of research, along with their primary advantages compared with traditional solvents, including low toxicity and cost, easy handling, biodegradability, biocompatibility and reusability [16].

In addition to this, there is a current need of producing eco-friendly materials for either feedstock and technologies. To some extent, membrane technologies demand more environmentally friendly materials for the synthesis of membranes. To date, it is likely that chemically synthesized polymers are among the main materials used for membrane manufacture, which represents an environmental issue due to their low biodegradability and their fossil-based origin. Even if the use of DESs in membrane science and technology, as testified by the data reported in **Figure 1**, is still at a seminal stage, the number of works in the field is constantly growing. In principle, a solvent, as a dissolving phase in the dope polymer solution, plays a crucial role in membrane manufacturing, determining changes in membrane properties (mainly structure) and consequently influencing its separation performance [17,18]. The use of DESs in membrane preparation can be, therefore, considered as an emerging and valid option in order to impart specific physicochemical properties to the membranes. Besides analysing the ongoing progresses that have been made on the use of DESs as solvents or additives in membrane preparation [19], this review also focuses on the various uses of DES in the post-modification treatments of membranes, in DES-liquid supported membranes and in DES-assisted membrane processes [20]. Interestingly, DESs are able to improve the

membrane's separation performance thanks to a facilitated molecule transport and/or an adsorption mechanism occurring through the functional groups borne in their chemical structure [21–23]. However, the compatibility of DESs and polymer phases aimed to the preparation of homogeneous membranes with a dense morphology, is still a challenge. Therefore, this review also illustrates the guidelines of using DESs for dense membrane fabrication, together with the advantages and drawbacks of such membranes when attending specific selective gas and solvent separations. To finalize, brief feedbacks on concepts and synthesis of DESs are also given, along with the core interactions identified by researchers between target molecules and DES phases for enhanced target molecules separation.

2. Brief background on the properties of DESs

DESs and ILs are considered as new types of green solvents. They share, in fact, several properties and advantages even if they are chemically quite different [24]. A typical DES is defined as a liquid system formed from a eutectic mixture of Lewis or Brønsted acids and bases. From a chemical perspective, DESs are synthesized by combining a hydrogen bond acceptor (HBA), like quaternary ammonium salts, with a hydrogen bond donor (HBD) compound (e.g., carboxylic acids, alcohols, sugars, amines, etc.) [25]. **Table 1** enlists a few typical examples of HBAs and HBDs agents used for the synthesis of DESs.

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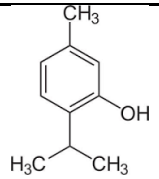
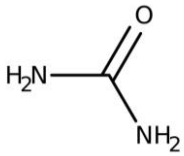
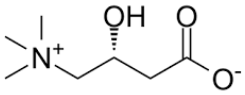
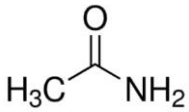
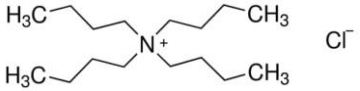
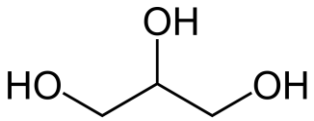
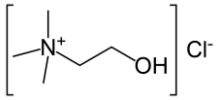
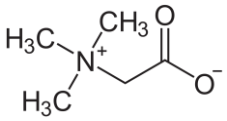
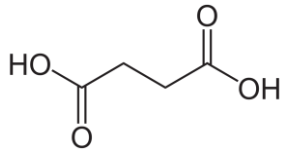
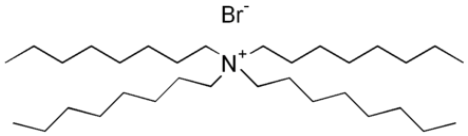
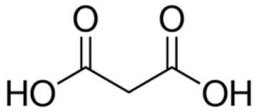
Table 1. Typical HBDs and HBAs agents used for the synthesis of DESs [1,26,27].

HBA	Chemical structure	HBD	Chemical structure
Thymol		Urea	
L-Carnitine		Acetamide	
Tetrabutylammonium chloride		Glycerol	
Choline chloride		Ethylene glycol	
Trimethylglycine		Succinic acid	
Tetraoctylammonium bromide		Malonic acid	

DES classification is largely depending on the nature of the element compounds and they are generally categorized in four types, as detailed in **Table 2** [1]. For example, DESs based on MClx and quaternary ammonium salts (*type I*) are recognized as an analogous type to the metal halide/imidazolium salt systems. When DESs present hydrated metal halides and choline chloride, they are recognized as *type II*. The low cost of the hydrated metal salts together with their inherent air/moisture stability makes them a good option in large-scale applications. Regarding *type III* DESs, they are formed from choline chloride and HBDs, which make them attractive due to their ability to solvate a number of transition metal species, including chlorides and oxides. To date, *type III* DESs are likely to be the most studied, presenting low cost, non-toxicity and biodegradability [28]. If transition metals can be incorporated into ambient temperature eutectics, these DESs are termed *type IV*. Particularly, metal salts would not commonly ionize in non-aqueous media but $ZnCl_2$, for instance, has been demonstrated to form eutectic mixtures with urea, acetamide, ethylene glycol, among others.

Table 2. Classification, general formula and terms of DESs [1].

Type	Formula	Terms
Type I	$Cat^+ X^- zMCl_x$	M = Zn, Sn, Fe, Al, Ga, In
Type II	$Cat^+ X^- zMCl_x \cdot yH_2O$	M = Cr, Co, Cu, Ni, Fe
Type III	$Cat^+ X^- zRZ$	Z = $CONH_2$, COOH, OH
Type IV	$MCl_x + RZ = MCl_{x-1}^+ \cdot RZ + MCl_{x+1}^-$	M = Al, Zn Z = $CONH_2$, OH

In DESs synthesis, hydrogen bonding is the main responsible to chemically join a HBA and a HBD [29], as graphically represented in **Figure 2a**. For instance, the new self-associated mixture displays a eutectic phase characterized by melting point value (T_m) lower than that of each forming molecule (see **Figure 2b**). This is a quite well-known phenomenon as the eutectic point represents the lowest temperature among all the individual compositions. Experimentally, most of the DESs

reported in literature display a T_m lower than 100°C [30]. Such a phenomenon occurs when two compounds with different molecular sizes are merged. Apart from this property, **Figure 2b** also describes some other interesting features of the new eutectic mixture, including good thermal stability, high tunability, high dissolubility, good chemical stability, among others. The physicochemical properties (such as acidity, viscosity, gas solubility, density, hydrophilicity/hydrophobicity, T_m, volatility) of DESs are greatly dictated by various factors, such as the type of HBA/HBD, the synthesis protocol and the operation parameters including the molar ratio, the temperature and the mixing time.

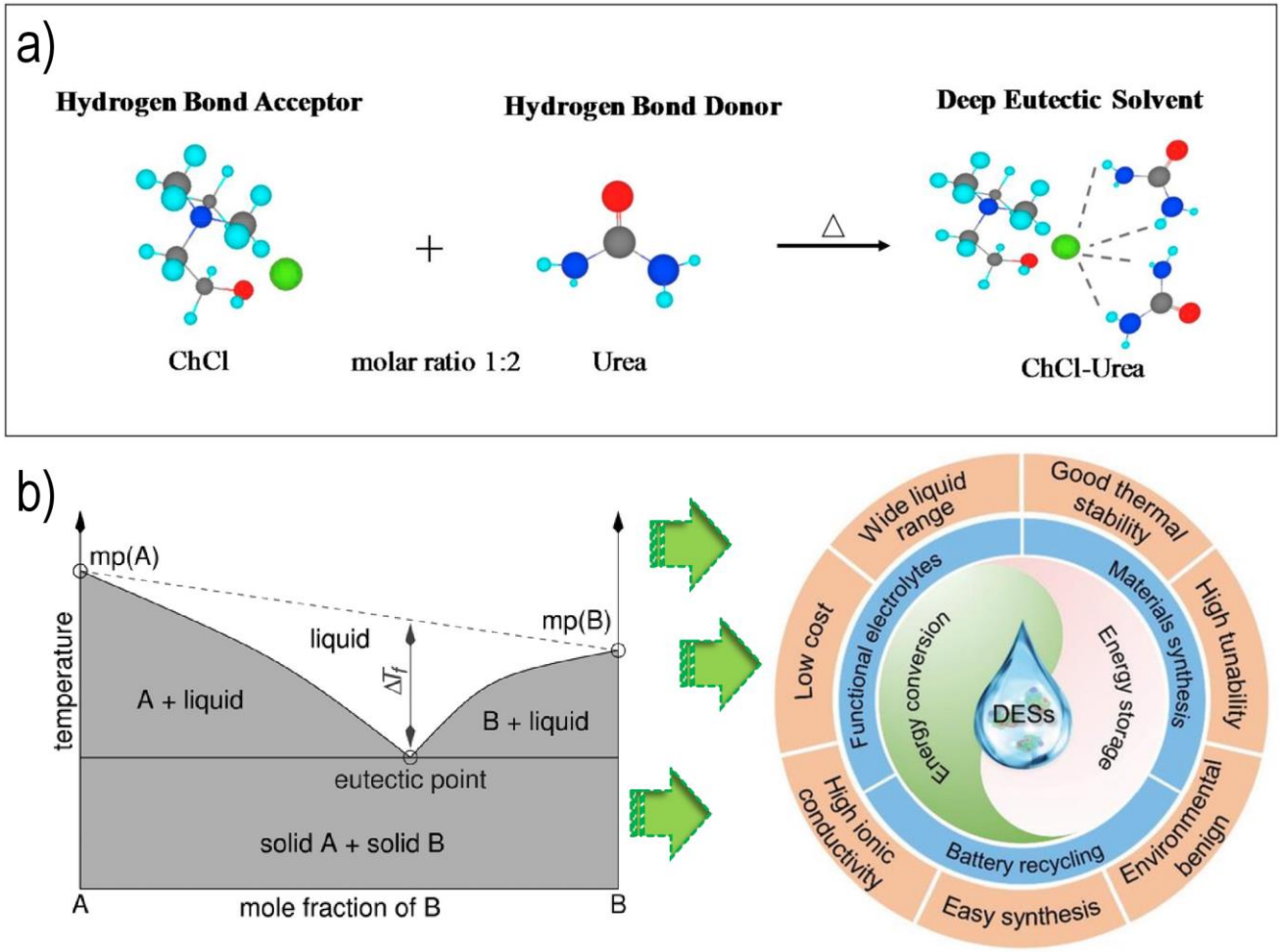


Figure 2. a) Graphical drawing of typical DES formation [30], and b) main features and properties of DESs including eutectic point on a two-component phase diagram [1].

In a polymer membrane containing DESs, both components (i.e., polymer and DES) can interact resulting in the following scenarios: i) the DES could act as a solvent only, ii) any of the DES elements (HBA or HBD) can be part of the polymerization, and iii) the DES can provoke significant changes in polymer properties, such as surface modification, morphological and structural changes [31]. At this point, the nature of DESs (i.e., hydrophilicity and hydrophobicity) is relevant when merged in membranes since specific membrane technologies (such as pervaporation, gas separation) require membrane surfaces with a hydrophilic or hydrophobic nature to differentiate polar and non-polar molecules [32,33]. As an example, hydrophilic pervaporation membranes preferentially transport polar solvent molecules (including water) hindering the permeation of less polar (or non-polar) molecules. On the contrary, hydrophobic pervaporation membranes preferentially transport less polar (or non-polar) molecules, retaining polar molecules. Here, the application of DESs and their nature should be smartly selected in order to accurately tune membrane properties facilitating the permeation of the target molecules.

Therefore, the next section is devoted to the different strategies so far employed in applying DESs in different scenarios of membrane technologies.

3. Breakthroughs on DES applications in membrane fabrication and DES-assisted membrane technologies.

3.1. DESs in membrane preparation and DES-polymer membranes

As in any polymer preparation protocol, a solvent is primarily required to create the dope solution and then to form a membrane using specific techniques, such as phase inversion (including solvent-induced, temperature-induced or vapour-induced phase separation), dense-film casting method, electrospinning and track etching [34,35]. For the preparation of ultrafiltration (UF) membranes, Jiang et al. [36] introduced various imidazole-based DESs, based on organic Cl, Br salts and organic imidazole (IM) molecules, as pore-former additives in polyethersulfone (PES) membranes using the phase inversion technique. In principle, a pore-former is used in membrane fabrication to promote the porosity and to enhance the membrane pore size resulting in more permeable membranes. Since water is typically used as a non-solvent during phase inversion, water-soluble pore-formers (like polyethylene glycol) are generally employed. They exhibit, in fact, hydrophilic groups which make them easily extractable by the formed membrane thanks to their solubility in the aqueous coagulation medium [37]. The same principle has been also explored in the case of hydrophilic DESs. Due to the affinity of the selected DES with water, the exchange rate between the solvent (e.g., NMP) and non-solvent (water) in the coagulation bath can be accelerated favouring the fabrication of membranes with a more porous architecture [19,36]. As shown in **Figure 3**, Jiang et al. [36] demonstrated that the incorporation of DESs, especially tetrabutylphosphonium bromide- imidazole (P_{4444}Br/IM), into the membrane matrix, can turn the pores into macrovoids in PES membranes; particularly, this was more evidenced when the DES concentration was increased from 0 to 2 wt.%. During filtration tests, the PES UF membranes exhibited a water permeability of 781 L m^{-2} h^{-1}, which was up to 6 times higher respect to the reference PES membrane not containing

any DES. At the same time, rejection tests revealed that bovine serum albumin (BSA) was minimally affected by DES incorporation since all the membranes presented a BSA rejection as high as 97.7%. According to the author's findings, such a high BSA rejection rate was the result of the narrowly distributed pore diameters, along with the reduction in the effective pore size. Moreover, by filtrating humic acid solutions, the water flux decline was found to be less pronounced and characterised by more stable performance. This suggested that DES based membranes can benefit of improved antifouling properties as a result of their lower surface roughness. These findings are in agreement with the ones documented by Maalige et al. [38], who treated film composite polyamide membranes with different DESs based on HBA (choline chloride) and HBD (ethylene glycol, urea and glycerol). The chemical surface modification considerably increased the permeation rate by 2-5 fold compared with the non-treated membrane with negligible changes in rejection. The enhanced measured flux was the consequence of an improved surface wettability obtained after the DES treatment; as observed by Jiang et al. [36], which also reported an increased surface smoothness for the membranes prepared with DESs. This result was attributed to the existence of hydrogen bonding between the DES and the polyamide moiety, which was confirmed by zeta-potential analysis [38]. By following a similar strategy, Vatanpour et al. [39] recently synthetised DESs based on ethylene glycol and choline chloride, the so-called ethaline, which was later proposed as a hydrophilic pore-former to fabricate PES/polyvinyl pyrrolidone (PVP) nanofiltration (NF) membranes. It was generally concluded that the use of ethaline led to a series of benefits in the resulting membranes, such as: i) the formation of uniform pores on the membrane surface, ii) the

creation of large macro-voids in the finger-like layer, iii) an enhanced surface smoothness, iv) an improvement in hydrophilicity, v) a high protein rejection and dye removal, and vi) a high permeation rate.

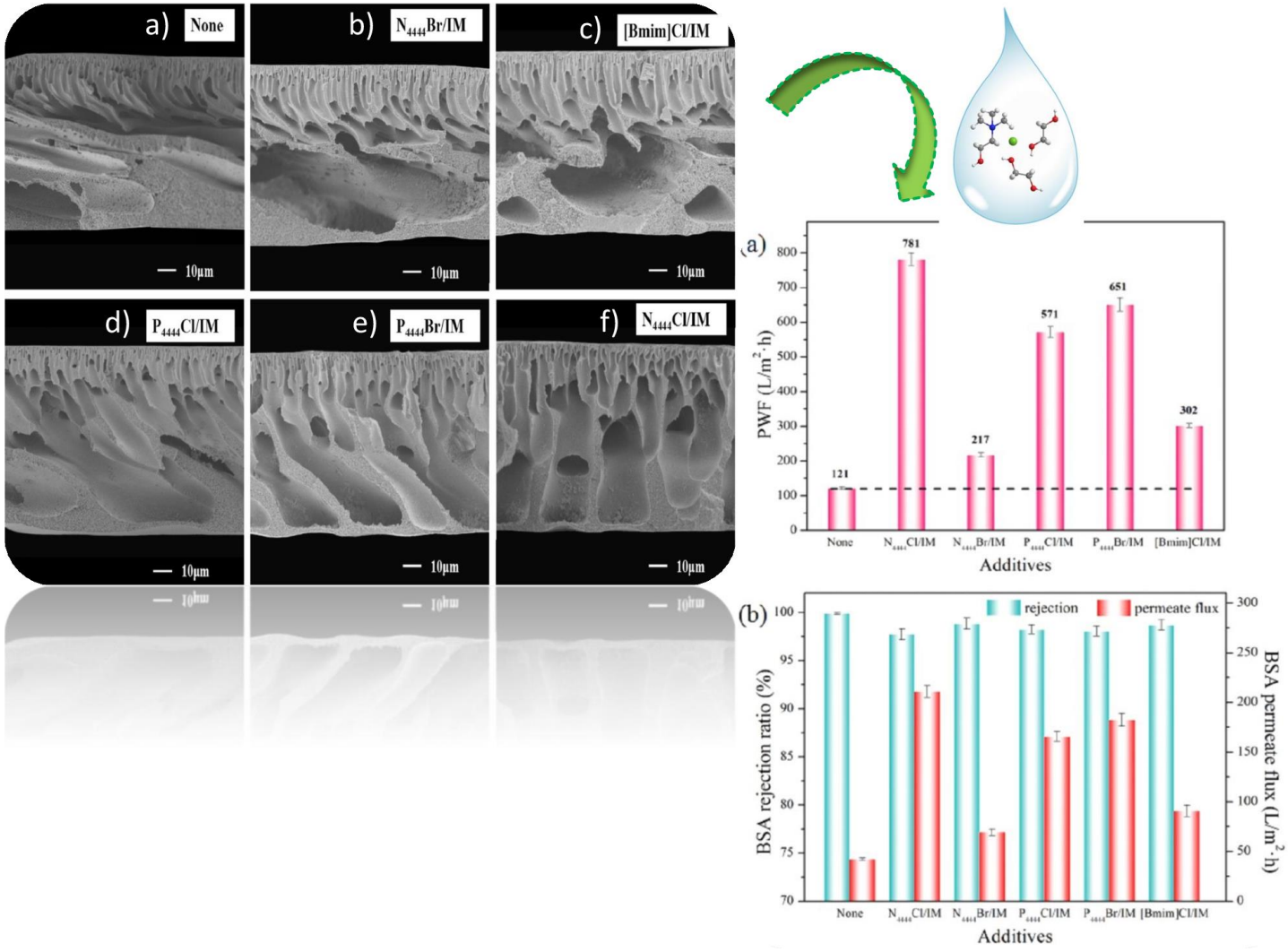


Figure 3. Morphological structure of PES UF membranes tailored by DESs as pore-formers; a) none, b) PES-N_{4444}4Br/IM, c) PES-[Bmim]Cl/IM, d) PES-P_{4444}Cl/IM, e) PES-P_{4444}Br/IM, f) PES-N_{4444}Cl/IM [36].

An outstanding application in preparing composite membranes was done by Kuttiani Ali [40], who utilized choline chloride-ethylene glycol (ChCl-EG) DES for the post-impregnation of silica nanoparticles that were subsequently embedded into polyimide UF membranes, as illustrated in **Figure 4a&b**.The impregnation of the DES on the nanoparticles was found to have a negligible effect on their morphology. The resulting DES-modified silica revealed an inter-spacing of 3.3 nm, while TEM analysis evidenced the existence of a porous shell comprising nanoclusters over the surface of the nanoparticles. According to the authors' speculation, such nanoclusters could be related to the DES in solid-state. A content of 2 wt.% of DES modified nanoparticles was found to be the optimal loading in the polymer matrix resulting in membranes with the best mechanical properties. In vacuum filtration experiments (at 85 kPa), the UF membranes doped with the nanofiller displayed high water permeation as high as 300 L m^{-2} h^{-1} and a rejection efficiency of 96% when applied for the treatment of a 30 mg L^{-1} of aqueous phenol solution. **Figure 4c** clearly describes the substantial effect of DES-modified silica into UF membrane compared with non-modified silica. Regarding the exceptional performance in terms of phenol removal, it was evidenced that the significant adsorption of phenol on the hydrated surface of the silica-polyimide membranes was due to hydrogen bonding and carboxylic moieties of polyimide. Additionally, hydrogen bonding between phenol and silanol and siloxane groups in silica surfaces could contribute to the efficient phenol removal.

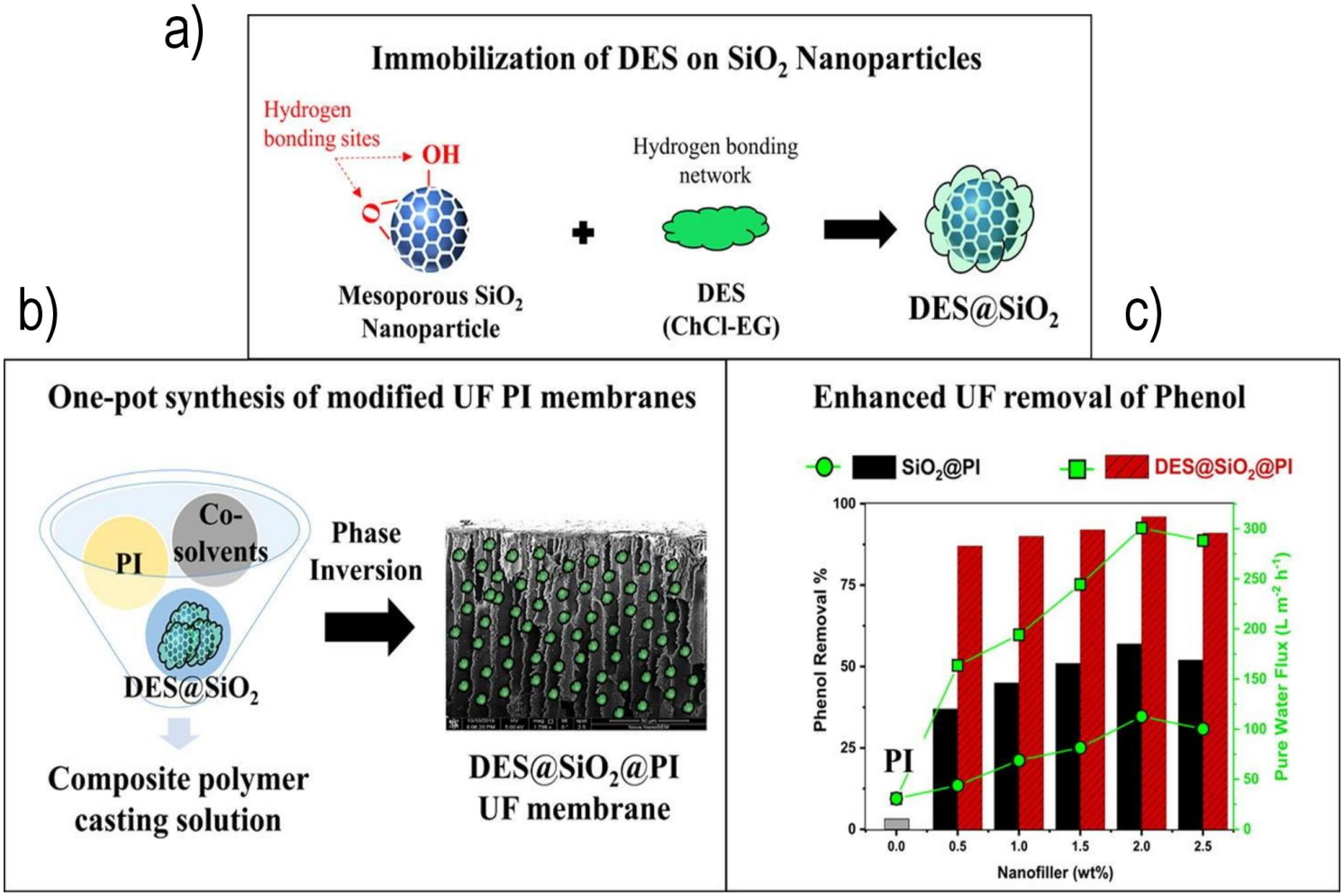


Figure 4. a) Immobilization of choline chloride-ethylene glycol (ChCl-EG) DES on SiO_2, b) embedding of DES impregnated silica nanoparticles into polyimide UF membranes, c) removal efficiency of phenol [40].

A DES based on urea and guanidine hydrochloride (molar ratio of 2:1) was used for the defined exfoliation of silk fibers (diameter between 20-100 nm and length between 0.3-10 µm) towards functional membrane preparation. In this work, Tan et al. [41] proved that the DES improved the exfoliation protocol of the fibers thanks to its ability to permeate into the silk fibers, loosening their structure and disrupting hydrogen bonds. This diminished the strength of the hydrophobic interactions in the silk. The resulting fibers showed better mechanical properties allowing to manufacture membranes for vacuum filtration testing. Here, the authors evaluated the ability of these membranes to remove ions, dyes, and protein considering the amphiphilic properties of the silk fibers. Membranes with a thickness of 18 µm exhibited a rejection efficiency of over 97% towards several dyes (e.g., Rhodamine B, congo red, methylene blue), along with exceptional protein uptake (over 96%); unfortunately, such membranes were not able to retain Cu^{2+}ions. In a subsequent work, Tan et al. [42] determined that silk protein nanofibers produced using a DES-assisted extraction protocol can be a promising alternative in tissue engineering applications since the fibers demonstrated exceptional cyto-compatibility, flexibility and mechanical stability.

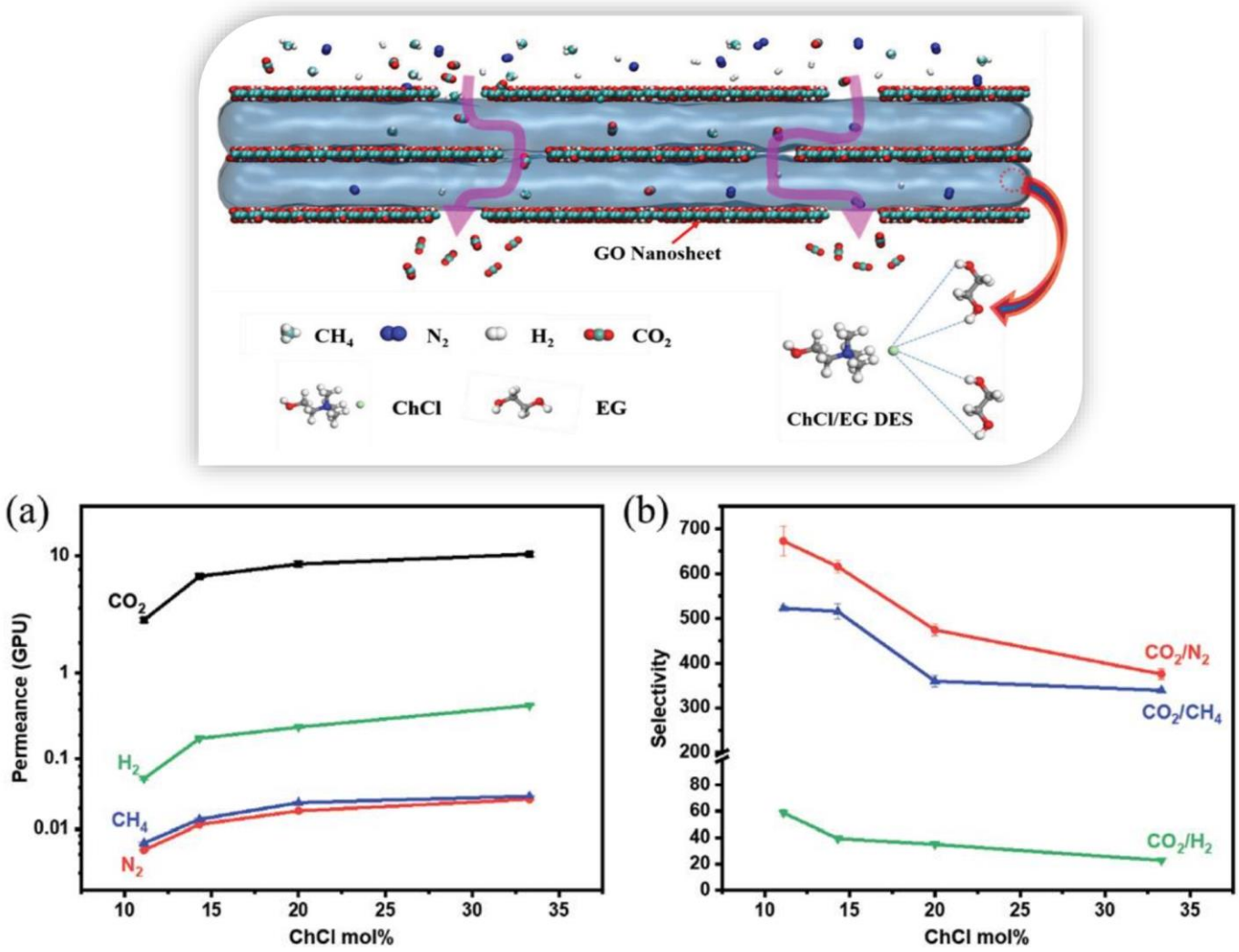
An important contribution of DESs relies on the facilitated water transport once incorporated in membranes. According to Seyyed Shahabi et al. [43], composite thin-film polyamide reverse osmosis membranes modified with choline chloride-urea (1 wt.%) increased the water permeation (up to 56 L m^{-2} h^{-1}) and salt rejection (over 96.4%) by 27% and 3%, respectively, in comparison with a pristine polyamide membrane. The improvement was attributed to the ability of the DES of tuning

surface membrane properties by enhancing their surface hydrophilicity and smoothness due to the presence of hydroxyl functional groups. Lately, ChCl-EG was systematically applied for the chemical functionalization of graphene oxide (GO) NF membranes [44]. The developed membranes were able to display unprecedented water permeability of 124 L m^{-2} h^{-1}, which represents a 5-7 times higher permeability compared with permeability of 22 L m^{-2} h^{-1} in unmodified GO membrane, and a high rejection toward salt and dyes (nearly 99%). Eventually, the DES provoked a great impact on the structural properties of GO in various scenarios: *i)* it shifted the d-spacing of GO, *ii)* it decreased their lateral size and *iii)* it decreased the wettability properties of the final membrane.

3.2. DESs in membrane preparation for gas separation and pervaporation

Membrane gas separation and pervaporation are among the most performing processes for the separation of gas and liquid phases. Both technologies require a continuous non-porous membrane to carry out the selective separation in the gas (or vapour) state [45,46]. In practice, the presence of porous structures and defects in the membrane matrix leads to a lack of the separation efficiency. Therefore, the suitable application of DESs in gas separation and pervaporation membranes is quite challenging. Nevertheless, researchers have implemented intelligent strategies in applying DESs in such technologies. For instance, Lin et al. [47] designed a CO_2-selective membrane by depositing ChCl-EG into GO nanosheets, as schematically represented in **Figure 5**. In this case, the replacement of the traditional ILs with their green analogues DESs

was successfully achieved; where the liquid DES phase considerably facilitated the CO_2 diffusion. After confirming the CO_2 selective properties, the authors varied the molar ratio of DES and membrane thickness finding exceptional CO_2 separation against light gases (e.g., N_2, CH_4 and H_2). Such parameters (molar ratio and thickness) were deeply evaluated since the molar ratio of HBA and HBD species greatly determines the physicochemical properties (solubility, viscosity, etc.) of the resulting eutectic mixture [48] and may influence the membrane performance, while the second parameter dictates, to some extent, the permeable properties of the resulting membrane [49]. In Lin's work, it was noted that the permeance of four gases increased as the choline chloride mole fraction increased (see **Figure 5a**), while the CO_2/light gas selectivity behaved oppositely (see **Figure 5b**). Even though the membrane containing a DES with molar ratio 1:2 offered the lowest selectivity, it still displayed a selectivity for CO_2/N_2, CO_2/CH_4, and CO_2/H_2 of 370, 339, and 23, respectively, proving its preferential CO_2 transportation compared with light gases. In this membrane concept, it was clear that the selective solution-diffusion mechanism across the DES-filled laminated GO (see **Figure 5**) took place. The CO_2 solubility and diffusion in DESs were not well described but it was speculated that intermolecular hydrogen bond dominates the CO_2 absorption in choline-based DESs. It is important mentioning that DESs were also able to improve membranes durability (in terms of long-term operation) and to enhance their thermal stability. The latter property was the result of the hydrogen bonding between the GO sheets and DES; for example, the hydrogen bonding attraction of GO for Cl^- and ethylene glycol induced the formation of Cl and ethylene glycol enriched layers which improved the final stability.



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242 **Figure 5**. Graphical drawing of ChCl-EG-deposited GO membrane; a) its CO_2 transport mechanism, and b) its separation

243 performance [47].

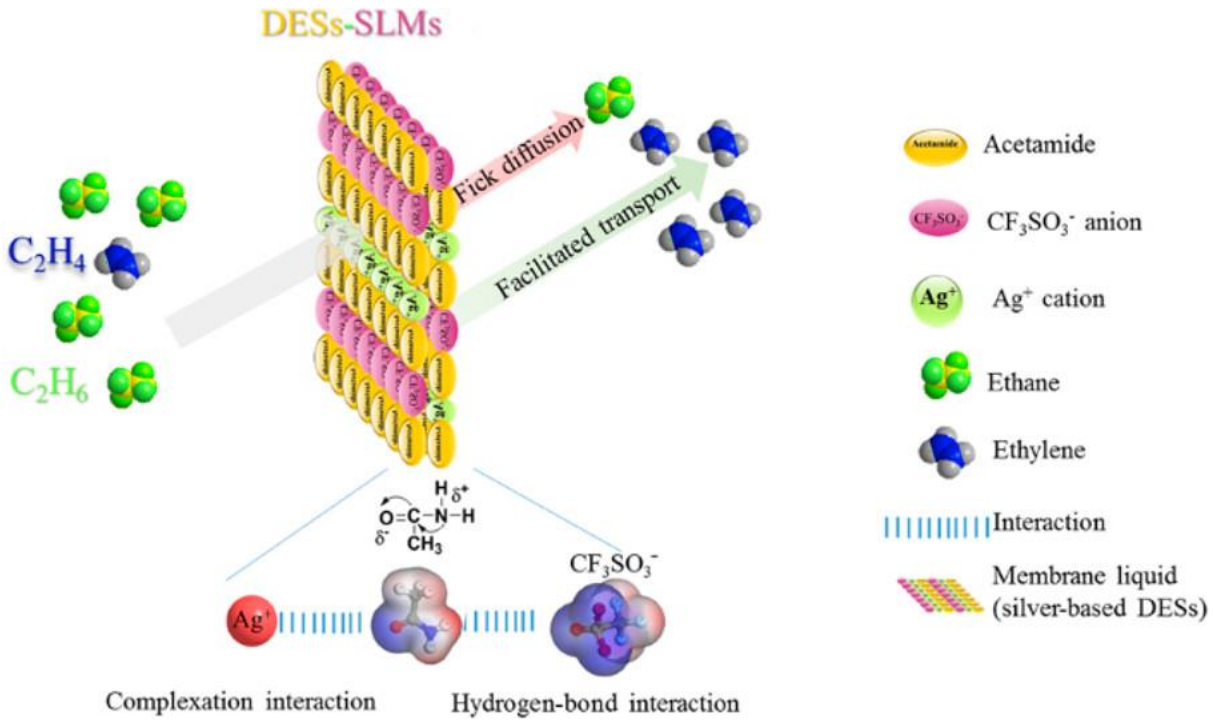
Using the same concept as Lin et al., DES-supported liquid membranes were fabricated by Saeed et al. [50]. Basically, Saeed and co-workers used betaine-based natural DESs that were embedded into a porous PVDF support. In the permeation experiments, the CO_2 permeability raised from 25 to 29 Barrer (10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} $cmHg^{-1}$) by replacing different HBD from tartaric acid to malic acid; but betaine stood as the dominant element with high solubility and diffusivity according to COO^-CO_2 interactions. Such carboxylate group (COO^-) is, in fact, recognized for its high CO_2 affinity [51]. Additionally, the ideal CO_2/CH_4 selectivity varied from 51 to 56 when tartaric acid was substituted by malic acid as the HBD. Very recently, Craveiro et al. [52] introduced choline chloride and urea (1:2) into a polytetrafluoroethylene (PTFE) support for CO_2 separation. This DES was selected according to its higher CO_2 solubility, which was accompanied by high permeability values (up to 100 Barrer). Van der Waals's interactions were the predominant forces formed between the gas molecules and the DES. By using choline chloride and levulinic acid (molar ratio of 1:2), de Castro et al. [53] also evidenced acceptable CO_2 permeability between 36-77 Barrer with good CO_2/N_2 selectivity (varying from 17 to 32).

Poly-DESs constituted by choline chloride (as HBA) and two different HBDs (such as polyacrylic acid and polyacrylamide) were prepared by Ishaq et al. [54], who sodden them into porous PVDF membranes for the potential CO_2 capture. The doped membranes showed a CO_2/CH_4 selectivity as high as 50 compared to pristine PVDF membranes; moreover, CO_2/N_2 selectivity was approximately 60. Both acceptable performances were linked to the basicity, molar free volume and the

hydrogen bonding strength of the DESs. In a current attempt aiming at producing new CO_2-selective membranes, Lin et al. [55] nanoconfined ChCl-EG (molar ratio of 1:4) into nanoslits of laminated MXene and later assessed their capacity of separating CO_2 from various lighter gases. Experimentally, the MXene supported DES membrane exhibited a CO_2 permeance of 26 gas permeation unit (GPU) (expressed as 10^{-6} cm^3 (STP) cm^{-2} s^{-1} $cmHg^{-1}$), with CO_2/N_2, CO_2/CH_4 and CO_2/H_2 selectivity values of 319, 249 and 12, respectively. In this case, the hydrogen bonding interactions guaranteed simultaneously the linking of DESs onto MXene and the CO_2 transport across the 2D material.

Towards different gas separation applications, metal chlorides into 1-butyl-3-methylimidazolium chloride- cuprous monochloride ([BMIM]Cl)/CuCl DESs were implemented to enhance the activity of the Cu^+ carrier for ethylene/ethane separation [56]. In fact, the authors have deeply analysed in a series of studies the complexation effect of several metals (such as Cu, Ag, Al) in gas transport properties of DESs [56–60]. In a first study, the initial impregnation of DESs into PVDF support membranes was performed, providing an ethylene/ethane selectivity of 17.8, which corresponded to higher values compared with the membranes without $ZnCl_2$ (displaying a selectivity of 10.7) [56]. The preferential permeation of ethylene through DES was the primary factor for the high membrane performance since ethylene gas molecules can positively interact with Cu^+ via π-bond complexation. According to the study, such DES-supported membranes presented stable long-term operation over 150 h. Concurrently, the same research group investigated a second DES, choline chloride/glycerol (molar ratio 1:2) dissolving CuCl, for the ethylene/ethane separation using liquid membranes [57]. At this time, the viscosity

276 and the strength of hydrogen bond networks were ascribed as the responsible variables for the facilitated transport of
277 ethylene in respect to the ethane molecules. In a more recent work, Jiang et al. [58] documented that ethylene/ethane
278 separation can be reached by confining a ternary DES (based on silver nitrate with the aluminium nitrate
279 nonahydrate/methylacetamide mixture with a molar ratio of 1:0.4:4) in a PVDF support. Here, ethylene selectivity was
280 tentatively fostered due to the complexing interaction between Ag^+ and methylacetamide, together with the complexing
281 interaction between Al^{3+} and NO_3^- that weakened the electrostatic interaction between Ag^+ and NO_3^-, apparently enhancing
282 the interaction energy between ethylene molecule and Ag^+ carrier (see **Figure 6**).



283

284 **Figure 6**. Facilitated transport mechanism in DES-supported membranes for gas separation [59].

285

286 This phenomenon was confirmed for olefin/paraffin separation as well [59]. When compared with the available literature, an
287 outperforming ethylene/ethane performance was stated due to the synergistic effect taking place in this system. It is
288 important to point out that the so-called complexation effect has been speculated between hydrophobic L-menthol/salicylic
289 acid and Ag^+ ions, forming a new complex transport species driven by the difference of concentration [61].

Until now, most research in gas separation has been directed towards DES liquid membranes; however, the chemistry related to the DESs may allow their complete merging into polymer phases. This is the case of Pulyalina et al. [62], who recently prepared polyamide-imide/DES composites using zinc chloride and acetamide (molar ratio of 1:3). In this regard, the proposed DESs were able to be blended in the polymer phase by hydrogen bonds. The membranes did not show any visible defect, interfacial voids or clusters in membrane morphology, offering the possibility for separating water-isopropanol (IPA) mixtures via pervaporation. Experimentally, the membranes, containing 10 wt.% DES, could dehydrate IPA showing total fluxes of 82 g m^{-2} h^{-1} and a separation factor of 216. On the other hand, the membranes with 5 wt.% of DES also demonstrated their ability in splitting gas pairs, such as O_2/N_2 and He/O_2, with separation factors of 15.9 and 19.7, respectively. The addition of the DES significantly increased the permeation and separation efficiency with respect to the pristine polymer membrane. In an atypical solvent separation, Dietz et al. [63] separated furfural and hydroxymethylfurfural from diluted aqueous solutions. Hydrophobic DESs composed of various HBDs (decanoic acid, thymol) and HBAs (lidocaine, thymol, n-tetraoctylammonium bromide, thymol) were immobilized in commercial membrane supports. The DES containing thymol/lidocaine (molar ratio of 2:1) and then supported in polyethylene was found to be the best candidate for the separation of furfural and hydroxymethylfurfural from water.

3.3. DESs in membrane preparation for electromembrane processes

An electromembrane process consists of a unit operation employing electric potential gradient as the driving force for ions transport. Currently, such membrane technique is proposed for the removal of charged components from solutions, e.g., for producing drinking water from brackish water. The pioneering applications of DESs in this field were carried out with the aim of improving the electrical conductivity of the membranes. In 2016, Rahman et al. [64] fabricated a polymer electrolyte based on poly(vinyl alcohol) (PVA) via electrospinning. The resulting electrospun membranes were immersed in N,N-diethylethanolammonium chloride/ethylene glycol DESs. This was systematically explored since there was evidence that the electrical conductivity of the DESs varied depending on the molar ratio. After soaking in DESs with a molar ratio of 1:2, the membranes demonstrated interesting electrical conductivity from 2.78×10^{-6} to 2.27×10^{-2} S cm^{-1}. Based on this finding, the authors suggested that such membranes could be good candidates for specific applications in batteries, sensors, energy storage, etc. In the line of enhanced proton conduction membranes, Wong et al. [65] found a significant improvement in the proton conductivity of chitosan/carboxymethyl cellulose blend membranes when containing choline chloride/urea (1:2). Particularly, the membranes (composed of 50 wt.% chitosan and DES) registered the highest proton conductivity of 1.57×10^{-2} S cm^{-1}, which was comparable with the commercial Nafion-117 membrane (ca. 8.6×10^{-2} S cm^{-1}). When dealing with electrolyte applications, this membrane could also be a good candidate since it showed low water uptake (ca. 49%), inferring a lower structural damage. Herein, DES contributed to preserve the chitosan membrane structure that could be

322 weakened by merging with carboxymethyl cellulose. The DES contribution was ascribed to the strong ionic interaction of its
323 oppositely charged ions with the polymeric chains, increasing the segmental mobility of the entire membrane [66].
324 DESs have not only been proposed to tune the properties of membranes but also as a liquid interface in electromembrane
325 technologies. For instance, Hansen et al. [67] reported the electromembrane extraction of six polar drug analytes (tyramine,
326 metaraminol, sotalol, ephedrine, atenolol and metoprolol) from drug-free plasma using non-ionic DES elements (such as
327 camphor, coumarin, DL-menthol, and thymol) as liquid interface. For this application, commercial PVDF filter membranes
328 of 0.45 µm pore size (96-well MultiScreen-IP filter) were used as support for the DESs. Depending on the type of DESs, the
329 electromembrane system offered a recovery efficiency that varied from 47 to 93% towards the drugs. In principle, the authors
330 defined that the obtained DESs were highly aromatic acting as strong HBDs and moderate HBAs. Interestingly, aromatic (π
331 type) interactions were identified for the transfer of bases, while hydrogen bonding was dominant for acids.
332 Karimi et al. [68] studied the effect of halogens on proton conductivity and fuel cell performance of Nafion membranes.
333 Bromide (Br^-) and iodide (I^-) based DESs were thus prepared and used as immersion phases for the membranes.
334 Experimentally, bromide-based DESs were likely to display the best conductivity of 337 mS cm^{-1}, which corresponded about
335 120% higher value than the iodide-based Nafion/DES membranes; they also showed a 1200 % higher conductivity than
336 other Nafion/IL polymer polyelectrolyte membranes at anhydrous conditions. The interaction between such DESs and
337 Nafion membrane is not well explained but it is believed that in Nafion/DES composite membranes, in presence of ethylene

glycol, sodium iodide (NaI) can interact with a sulfonic acid group of Nafion ($R–SO_3H$) to yield $R–SO_3Na$. Thus, the existence of I^- in Nafion/DES solution can be a consequence of a hydroiodic acid reaction with available oxygen (O_2). Nevertheless, when any DES is attempted to be used as proton conductive media in polymer membranes, some criteria should be carefully taken into account [69], such as:

- DES may present the ability to dissociate protons from sulfonic acid groups of sulfonated polymers (like Nafion);
- Low DES viscosity;
- DES proton conductivity;
- Outstanding DES thermal stability;
- A feasible mechanism for DES addition to a polymer matrix.

Such criteria were suggested by Karimi et al., continuously exploring the improvement of properties of Nafion membranes. These membranes are probably the most prominent commercial cation exchange membranes for electrochemical applications [70]. In comparison to bromide-based Nafion/DES membranes that exhibited a conductivity of 337 mS cm^{-1} [68], iodide-based Nafion/DES membranes tend to offer lower proton conductivity (ca. 153 mS cm^{-1}) [69]. Although Nafion/DES membranes owned superconducting properties as a consequence of a Grotthuss-like mechanism for proton conduction, Karimi et al. [71] also observed that the presence of water can either have a constructive or destructive effect on the DES and Nafion/DES membranes, pointing out that such factor could be determinant in the performance of a polymer

electrolyte membrane. It is worth mentioning that the Grotthuss mechanism (or proton jumping) is the process in which an 'excess' proton or proton defect diffuses through the hydrogen bond network of water molecules or other hydrogen-bonded liquids [72].

3.4. DES assisting membrane processes and extraction techniques

Since DESs have proven their exceptional ability for extracting various types of solutes [6,73], they have been also involved in assisting extraction protocols. A successful approach based on the extraction of amino acids, by filling DES into the pores of commercial membranes, was obtained by Li et al. [74]. In this work, the process consisted of two independent diffusion cells, in which the membranes had direct contact. After evaluating several DESs, choline chloride/p-toluene sulfonic acid was the most effective (efficiency of 86.1%) in extracting tryptophan, pointing out the hydrogen bonding (between the DES and the amino acids) as the driving mechanism. In another work, Matsumoto et al. [75] developed lactic acid permeable polymer inclusion membranes (PIMs). At this point, DESs were prepared based on various HBDs (such as urea, glucose and several organic acids) and HBA (such as choline chloride, lidocaine, DL-menthol). The investigated DESs were combined with poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and polyvinyl chloride (PVC). Interestingly, some of the DESs were water-soluble suggesting an important role as transport carriers, contributing to possible polar interactions (e.g., hydroxyl groups) between the membrane and the lactic acid for its permeation.

A new DES membrane-based microextraction protocol was developed by Shishov et al. [76], who strategically extracted analytes due to *in situ* DES formation between analytes and choline chloride (as HBA) supported in a hydrophilic poly (vinylidene fluoride-co-tetrafluoroethylene) membrane. The HBA promoted the extraction of phenolic compounds (such as guaiacol, eugenol, isoeugenol, among others) from food samples and concurrently formed DESs, which resulted in an extraction recovery rate ranging from 70 to 80%.

4. Concluding remarks and future directions in the field

This review evidenced that the major application of DESs in membrane preparation deals with their use as pore former additives for porous asymmetric membranes. The resulting membranes have displayed different properties, tuned pore size, enhanced surface wettability and hydrophilicity, leading to outperforming permeation rates with no decline in membrane rejection. However, specific nanomaterials (e.g., silica nanoparticles) can also be impregnated by DESs tuning the performance properties once embedded in polymer composites. Furthermore, DESs have been also used in the preparation of DES-supported polymer membranes, proving greater effect than the conventional IL membranes in gas separation (CO_2, ethylene, etc.). At this point, the complexation effect between metals (such as Cu, Ag Al) and gas molecules (ethylene, olefin) has been identified as the main mechanism for enhancing gas transport properties of DESs [56–59]. A few reports, but relevant, have demonstrated that a smart selection of DESs, according to their properties, can also be the key for the

preparation of defect-free dense membranes suitable for gas separation and pervaporation applications [47,62]. Regarding the preparation of membranes for electromembrane processes, DESs demonstrated to enhance the proton conductivity of commercial Nafion membranes by soaking them into the DES matrix. Also, DESs have assisted specific extraction and purification processes based on membrane processes thanks to their selectivity and exceptional analyte transport. By analyzing the current state of the art of DES application in membranes and membrane processes, the future directions and suggestions for the new researchers in the field are given as follows:

- Innovative DESs, e.g., based on protonated L-proline (as HBA) and glucose/xylitol (as HBD) [77], have been ultimately prepared by the research community. According to their natural components, they present a great potential in multiple applications (e.g., food, pharmaceutical industry, etc.) including membrane fabrication which have never been explored so far. It is quite possible that novel DESs could be applied due to their success in other chemical engineering applications [6,10]. Importantly, the molar ratio of HBA and HBD elements will inherently be studied since such a relationship strongly influences the resulting features of the eutectic mixture.
- In specific water separations using membranes, DESs have shown great outcomes thanks to the facilitated water transport related to the DES's polarity. However, the latter property is difficult to be defined in a DES and challenging to express quantitatively [78]. Here, it is likely that membranes will profit more from hydrophilic DESs associated with their polarity. On the contrary, when using hydrophobic DESs, the strength of hydrogen bonding will be determinant

402 in selective water transport [79].

403 • When DESs are attempted to assist specific extraction and purification processes using membranes, particular
404 emphasis should be paid to the possible interactions that water content may display on DES and target biochemical
405 molecules [80].

406 • To date, DESs have been successfully utilized for the preparation of porous membranes for pressure-driven
407 membrane processes. At this point, there are no reports of utilizing DESs as pore formers for the fabrication of porous
408 membranes for other membrane operations, such as membrane distillation [81], which requires porous membranes
409 with improved anti-wettability properties.

410 • As a suggestion for the new researchers in the field, it is recommended to be focused on synthesizing new CO_2-
411 selective DESs since the CO_2 capture is one the most investigated and attractive process in membrane gas
412 separation. Here, specific DESs (e.g., choline chloride/glycerol) have been identified as the new generation of CO_2
413 sorbents [82].

414 • As a current research gap, the study of the complexation effect of new DESs (such as L-menthol/salicylic acid) in the
415 transport of specific molecules should be further analyzed. Even though there is evidence that DESs can selectively
416 promote the transport of metal ions (Ag^+ ions) [61], it is needed to unveil and establish the real transport mechanism
417 of species through DES to open up the field to new applications.

- Thanks to the application provided by Mehrabi et al. [44], DESs have opened up the possibility to chemically functionalize inorganic nanomaterials that are currently sought for their outperforming water transport. Here, DESs can tune and define the interlayer spacing (i.e., *d*-spacing) and lateral size of 2D materials (such as GO, MXene) for superior performing membranes in water purification [83], solvent dehydration [84], seawater desalination, among others.
- The biggest interest is related to application of DESs at their eutectic point composition – optimisation of membrane performance should include studies also for other molar ratios which could offer more advantageous properties.
- DESs are formed by weak (hydrogen bonding) interactions. Their components can be soluble in the feedstocks subjected to desired separation process. Although high selectivity and throughput of the membranes, the risk of cross-contamination (DESs components leaching issues) into the purified feed in every study should be evaluated.
- Obtained DES based membranes should be always studied for minimum 5 consecutive cycles for a real assessment of performance stability.
- Especially in the case of natural DESs used for membranes preparation, the aspects related to their biodegradability should be taken into consideration. They relate to a positive disposal of the membranes after their usage, but also to the risks related to their performance instability in case of treatment of aqueous solutions that can contain bacteria able to degrade DES components.

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Conflict of Interest

The authors declare no conflict of interest.

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