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Perspective

Eutectogels: The Multifaceted Soft Ionic Materials of Tomorrow

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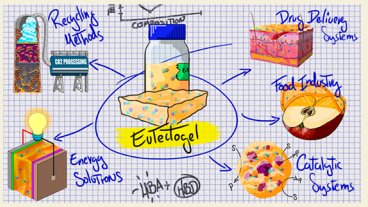
ABSTRACT: Eutectogels, a rising category of soft materials, have recently garnered significant attention owing to their remarkable potential in various domains. This innovative class of materials consists of a eutectic solvent immobilized in a three-dimensional network structure. The use of eco-friendly and cost-effective eutectic solvents further emphasizes the appeal of these materials in multiple applications. Eutectogels exhibit key characteristics of most eutectic solvents, including environmental friendliness, facile preparation, low vapor pressure, and good ionic conductivity. Moreover, they can be tailored to display functionalities such as self-healing capability, adhesiveness, and antibacterial properties, which are facilitated by incorporating specific combinations of the eutectic mixture constituents. This perspective article delves into the current landscape and challenges associated with eutectogels, particularly focusing on their potential applications in CO_2 separation, drug delivery systems, battery technologies, biocatalysis, and food packaging. By exploring these diverse realms, we aim to shed light on the transformative capabilities of eutectogels and the opportunities they present to address pressing industrial, academic, and environmental challenges.



KEYWORDS: *Eutectic solvents, Eutectogels, CO_2 separation, Drug delivery, Batteries, Biocatalysis, Food packaging*

1. INTRODUCTION

Eutectogels are a class of soft materials in which traditional eutectic solvents or deep eutectic solvents (DES) are embedded in a three-dimensional network, resulting in a stable, nonflowing, and self-supporting structure. These materials have gained significant attention due to their unique combination of properties from DES, such as low volatility, biocompatibility, cost-effectiveness, and ionic conductivity, as well as the versatility of gel networks, which provide flexibility and stretchability. This combination leads to highly tunable systems suitable for various applications, including energy storage, biomedicine, and environmental sustainability. The growing interest in eutectogels is fueled by their enhanced ionic conductivity, thermal stability, and adaptability, making them particularly valuable for advanced uses like solid-state batteries, drug delivery, and CO_2 capture.[1,2] As a fundamental component of eutectogels, the conceptual definition of classical eutectic solvents and DES is addressed in detail in Section 2.

Compared to conventional gels such as hydrogels, organogels, and ionic liquid (ILs) gels (iongels), eutectogels offer distinct and significant advantages in various scenarios, particularly regarding stability, functionality, environmental sustainability, and cost-effectiveness.[3]

Hydrogels, composed primarily of water embedded in polymer networks, are valued for their biocompatibility and moisture content.[4] However, they face limitations such as susceptibility to evaporation, reduced mechanical stability, and low ionic conductivity. These issues make hydrogels unsuitable for environments with low humidity or nonaqueous settings and are prone to freezing, damaging their structure.[5,6] In contrast, eutectogels benefit from the nonvolatile nature of eutectic solvents, providing enhanced stability and durability. This allows them to maintain their functionality and structural integrity even in dry conditions or over extended periods, making them a more versatile and reliable option than hydrogels.[7]

Organogels, which host organic solvents instead of water, provide better thermal stability compared to hydrogels and are useful in harsh environment applications where water-based gels would fail.[8] However, organogels pose significant challenges due to the toxicity and environmental hazards of many organic solvents. These concerns limit their use, particularly in biomedical and food-related applications, where safety and environmental impact are key considerations.[9] This makes eutectogels more environmentally friendly and suitable for a broader range of uses, including those requiring safe interaction with biological systems or food products.[10,11]

Iongels are known for their high ionic conductivity and excellent electrochemical stability, which make them suitable for applications like energy storage, catalysis, and advanced sensing technologies.[12,13] However, iongels are often expensive

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and can be challenging to synthesize, with some formulations raising concerns about toxicity and environmental persistence.[14,15] This limits the large-scale and long-term use of these soft ionic materials, particularly in applications requiring cost efficiency and sustainability. In contrast, eutectogels are a cost-effective alternative to iongels because eutectic solvents are generally cheaper and easier to produce while maintaining excellent ionic conductivity, making them a more sustainable and scalable option for various applications.[16]

Beyond these specific comparisons, eutectogels offer additional advantages over other soft gel materials. The ability to fine-tune the hydrogen bond donors (HBD) and hydrogen bond acceptors (HBA) within the DES gives eutectogels unparalleled customizability.[17] This allows researchers to design eutectogels with precise physical, chemical, and mechanical properties suited to specific applications, improving CO_2 capture efficiency,[7] enhancing drug delivery systems,[18] or optimizing solid-state electrolytes for batteries.[19] Moreover, the self-healing properties often observed in eutectogels, due to the dynamic interactions between DES components and the polymer network, provide added resilience and durability, which are not commonly found in other gels.[20−23]

Eutectogels can be classified based on how the polymer network is constructed within the DES medium.[2,7,24] In one of the most used approaches, DES functions as "inert" solvents, capable of dissolving cross-linkers, initiators, and monomers, which lead to covalently cross-linked polymer structures.[1] For instance, acrylic acid−based eutectogels cross-linked with poly(ethylene glycol) diacrylate have been prepared using polyols and urea/ChCl eutectic solvents.[25] On the other hand, supramolecular eutectogels can be formed by self-assembling a low molecular weight gelator (LMWG), typically an organic compound with a molecular weight below 2000 Da.[26] These materials have garnered considerable attention due to their rapid and straightforward preparation process and their thermal reversibility. For instance, supramolecular eutectogels were recently reported based on ChCl/polyols and a series of D-glucose acetal gelators.[27] On the same line, a solvent-exchange strategy has been proposed recently to prepare poly(vinyl alcohol) (PVA) eutectogels.[28] In this approach, interactions between polymer chains are first weakened by dissolution in water, followed by DES replacement, inducing PVA crystallization and the formation of a strengthened homogeneous network. Several authors have also classified eutectogels based on polymerizable deep eutectic solvents (PEDES), where DES serves as the medium and one of their components as a reactive monomer. However, considering that the liquid state is lost after polymerization, they can not be labeled as gels, and the term liquid-free or dry elastomers has been adopted for these materials.[29]

Building on the benefits of eutectogels, as researchers continue exploring novel DES formulations and polymeric scaffolds, these soft materials can revolutionize fields such as energy storage, biocatalysis, and advanced healthcare technologies, positioning them as a hot topic in materials science. In this perspective, we will provide an overview of the current challenges of eutectogels in the areas of CO_2 separation, drug delivery, batteries, biocatalysis, and food packaging.

2. THERMODYNAMIC FUNDAMENTALS OF EUTECTIC SOLVENTS

The term "eutectic solvent" dates back to the 19th century, credited to F. Guthrie's exploration of the "Eutexia" phenomenon. This phenomenon involves mixtures of two or more components exhibiting a minimum melting temperature at a specific composition known as the eutectic point.[30] It is now understood that all mixtures of pure compounds, whether entirely or partially immiscible in the solid phase but miscible in the liquid phase, display a cryoscopic descent.[31] In 2003, Abbot et al. introduced the term "deep" in DES by reporting an abnormally large depression in the melting point of a mixture denoted *"reline"*. This eutectic system was composed of ChCl with a melting point of around 302 °C, and urea with a melting point near 133 °C, leading to *reline* with a melting point of 12 °C.[32] DES are nowadays considered a unique mixture containing two or more components, with at least one serving as a HBD and another as a HBA.

Recently, machine learning has been successfully applied to predict the behavior of new DES combinations, enabling the design of eutectogels with tailored properties such as extended stability and environmental responsiveness.[33] Leveraging these predictions reduces the need for extensive lab testing, thereby accelerating development and lowering costs. Notable examples include predicting the electrical conductivity of DESs using quantitative structure−property relationships (QSPR) combined with artificial neural networks,[34] forecasting viscosity,[35] and predicting solid−liquid equilibrium diagrams for the development of new DES.[36] However, there remains a lack of clarity in the field concerning the distinctions between traditional eutectic solvents and DES, and it is crucial to establish a clear definition for these innovative systems.

A starting point was proposed by Couthino et al., who defined DES from a thermodynamic point of view as eutectic solvents that exhibit strong enthalpy-driven negative deviations from the ideal liquid mixture, as seen in *reline*, which displays asymmetrical deviations in the urea liquidus curve.[31,37,38] In general, for a binary mixture of components A and B, negative deviations arise when the interactions between A and B are stronger than the interactions within the pure components themselves (A-B > A-A, B−B). The eutectic system thymol/menthol is a true example of a DES (Figure 1). Consequently,

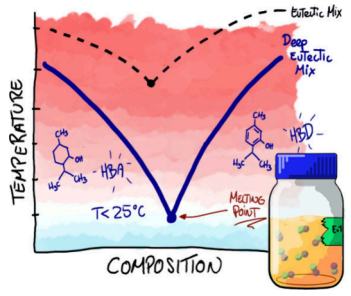

Figure 1. Schematic representation of the solid−liquid equilibrium phase diagram of an eutectic mixture and a deep eutectic mixture taking the case of menthol (HBA) and thymol (HBD) system showing strong negative deviations form the ideality.

substantial deviations from the thermodynamic ideality can result in mixtures with lower melting points, thereby providing unique liquid environments. Based on this, some archetypical DES, such as *ethaline*, should simply be labeled eutectic solvents because they have been demonstrated to behave as ideal binary mixtures.[39,40] Therefore, if we hold to the thermodynamic definition of DES, the scientific community must revise the indiscriminate use of the term "deep" in many

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eutectic systems without knowing their solid-equilibrium phase diagrams.

Despite these endeavors, a crucial question persists: To what extent must the magnitude of the negative deviations be reached for the eutectic mixture to qualify as a DES? To address this concern, van den Bruinhorst and Costa Gomes recently introduced an empirical descriptor (D_e) to categorize DES by quantifying the eutectic depth.[38] This represents a significant initial step, but a predetermined threshold value must be established to fully differentiate DES based on D_e. In our opinion, it would be judicious to return to the fundamentals and simply refer to all mixtures, regardless of whether they exhibit considerable negative deviations from ideality, as eutectic solvents (ES). After all, the essential aspect of these mixtures is their ability to remain liquid at a desired operational temperature. This ultimately enables the creation of tailored solvation environments and fosters novel chemical reactions when eutectic systems are used as solvents. Beyond this point of view, Prof. Sangoro et al. have recently suggested that there is more than thermodynamic fundamentals behind DES, revealing an interplay with dynamics in determining the properties of these systems.[41]

Another aspect that has been debated in the literature is that many mixtures labeled as DES undergo vitrification over a broad composition range, even at low heating and cooling rates. In other words, they undergo vitrification and exhibit a glass transition temperature (T_g) rather than a melting point. In such cases, the thermodynamic definition of DES becomes less relevant, as building accurate solid−liquid equilibrium phase diagrams can be pretty tricky. Some researchers have suggested using the term low-transition-temperature mixtures (LTTMs) to describe these mixtures.[42] Nevertheless, we decided not to make such a distinction for the purpose of this perspective, and from now on, we will refer to eutectics as ES regardless of whether they show a negative deviation from the ideality or undergo vitrification.

The capability to tailor key properties of ES, such as vapor pressure, thermal stability, ionic conductivity, and biodegradability, by selecting different components and adjusting their ratios makes them versatile and promising alternatives for a wide range of applications, such as drug delivery, chemical synthesis, extraction processes, and as electrolytes in batteries and capacitors.[43−47] Immobilizing these neoteric solvents into solid scaffolds affords an innovative class of soft materials called eutectogels, which have recently emerged with tremendous technological potential.[1,48] These materials share the fundamental features of ES and additional functions, such as stretchability, self-healing ability, and adhesiveness.[49] The versatility and unique properties of eutectogels have broadened the application scope of ES across various fields.[19,20,50−52]

3. EUTECTOGELS FOR CO_2 SEPARATION

Carbon dioxide is widely recognized as a key contributor to the "greenhouse" effect and to global warming. One of the most popular approaches for CO_2 capture is chemical absorption using aqueous solutions of alkanolamines, such as monoethanolamine.[53] However, this approach has significant drawbacks, including the corrosive nature of the reaction environment, solvent loss due to volatility, and high energy requirements for regeneration.[54] Alternatively, membrane separation is considered a cost-effective technology to mitigate the emission of CO_2 and alleviate its presence in the atmosphere.[55] Over the past few years, extensive efforts have been devoted to the development of membranes based on ILs,[56] especially in the realm of iongels, a class of soft solid materials containing high IL content.[57,58] Although different types of gelators have been adopted for the preparation of iongel membranes, a trend in this field is the formation of cross-linked iongels by mixing ILs with a monomer or oligomer, followed by free radical polymerization.[59−61] These materials exhibit high CO_2 permeability and good CO_2/N_2 selectivity properties.[62−64]

Despite their potential, the use of most ILs presents certain challenges, such as high cost and toxicity, which limit their widespread application on a technical scale. To overcome these limitations, ES are presented as a viable alternative because of their straightforward synthesis, low cost, and toxicity, which puts them at the forefront of current research (Figure 2).

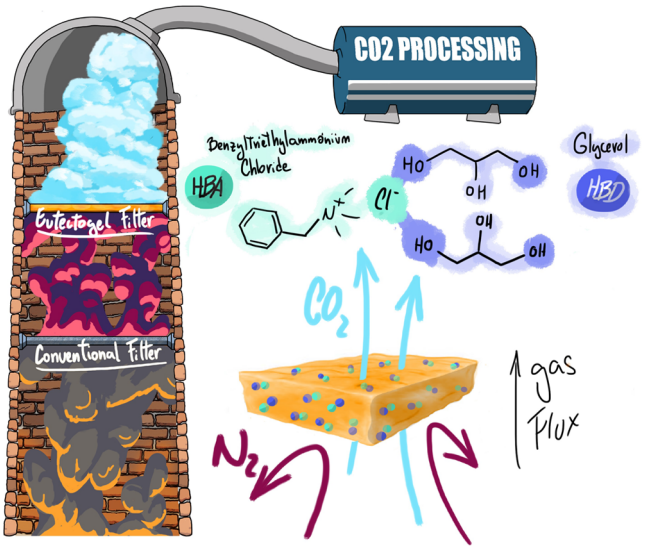

Figure 2. Schematic representation of eutectogels for CO_2 separation applications.

In contrast to iongels, which have attracted significant attention and have found application in CO_2 separation membranes, eutectogels have been little studied for this application. This disparity may stem from the predominantly hydrophilic nature of most ES employed so far or the potential evaporation of the components from the gel matrix under certain pressure and temperature conditions.[65] Interestingly, analogous to poly(ILs), poly(ES) formulations overcome the limitations of ILs and present interesting CO_2 permeability and selectivity values. Ishaq et al. developed poly(poly(acrylic acid)/polyacrylamide-ES) impregnated into microporous polyvinylidene fluoride membrane for CO_2/N_2 and CO_2/CH_4 separations.[66] Similarly, poly 1-butyl-3-methyl-imidazolium bromide ([Bmim]Br)/diethylene glycol-ES) was blended with poly(vinylidene fluoride) to form a membrane for selective separation of SO_2 from N_2 and CO_2.[67] Eutectogels consisting of betaine/glycerol ES and 12-hydroxystearic acid were also tested for flue gas desulfuration.[68]

Additionally, ES based on ChCl has been confined to multiple layers or membranes and proven to be capable of CO_2 separation. Lin et al. nanoconfined ChCl/ethylene glycol into graphene oxide. The resulting membrane exhibited not only effective CO_2 separation but also boasted excellent heat stability and long-term endurance.[69] In line with this, the

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incorporation of ChCl/ethylene glycol into nanoslits of titanium carbide ($Ti_3C_2T_x$) formed a membrane that exhibited high CO_2 permeance and effective CO_2/N_2 and CO_2/CH_4 separation. This membrane also showed excellent thermal stability and increased long-term endurance.[70] On the other hand, supported liquid membranes using ES have also demonstrated potential for facilitated olefin transport. In particular, silver-based ES consisting of $AgCF_3SO_3$ and CH_3CONH_2,[71] and ES containing NO_3^-,[72] were designed and used to fabricate membranes with good separation performance and stability for ethylene/ethane separation.

A crucial factor in developing competitive eutectogel membranes compared to IL-based membranes is the careful selection of the characteristics of the ES used. The solubility of CO_2 can be inferred from the size of the cation in the salt, which acts as HBA. ES with HBA combined with a larger cation, such as tetrabutylammonium chloride and tetraoctylammonium chloride, possess a higher CO_2 absorption capacity than those with a smaller cation, such as tetraethylammonium chloride and tetramethylammonium chloride, given the higher free volume of the sorbent with longer chain lengths.[73−76] Moreover, the nature and symmetry of HBA should be considered. For instance, ester or carboxylate groups can interact with CO_2 and improve its solubility,[77] while exchanging ethyl by benzyl group in an ammonium quaternary HBA results in lower CO_2 absorption capacity.[74] In turn, the nature of HBD determines the interaction between the ES and CO_2: using amines or alkanolamines results in chemical absorption, whereas glycols, sugars, and acids are responsible for the physical absorption of CO_2.[78] The number of moieties and the distance between them also play a role in CO_2 absorption. The presence of functional groups such as OH that are closer between them in butanediol-based ES,[79] as well as a significant number of ether groups in ethylene glycol-based ES or amine groups in amine-based ES, enhanced the CO_2 absorption.[80,81] The strength of the interaction between the HBD and CO_2 follows an order depending on the functional group (amide > carbonyl group > ether bond > hydroxyl group).[82] The molar ratio of HBA/HBD has diverse impacts on CO_2 solubility but does not follow a linear trend and depends on the structure of HBD.[75,79,80,83] Nevertheless, employing an ES with low viscosity is generally advised to obtain lower diffusion resistances and thus increase solvent fluidity, which ultimately leads to improved mass transfer.

Concerning the membrane matrix, diverse polymers are easily available and are generally preferred because of their low cost and desirable flexibility.[84] Given the similarities between ES and ILs, we believe that exploring the potential of polymers already used with ILs is a good starting point. For instance, commercial polyacrylonitrile membranes could be an excellent matrix material for load with ES.[85] Poly(ethylene glycol) diacrylate, polypropylene, polyvinylidene fluoride, nylon, and polyethersulphone could also be evaluated.[86−88]

So, selecting suitable ES and polymers is crucial in designing eutectogel membranes for CO_2 separation. Key considerations include the solubility of CO_2 in the ES, the compatibility between the solvent and the polymer, and the ability of the polymer to form a stable, cohesive membrane structure. A good example is the combination of betaine/urea with polyvinylidene fluoride, which has been shown to produce a eutectogel membrane with excellent CO_2 permeability and selectivity, thanks to the strong hydrogen bonding and ionic interactions within the membrane matrix.[89] In terms of CO_2 separation performance, studies have shown that eutectogel membranes based on polyvinylidene fluoride with betaine/urea,[89] ChCl/tartaric acid,[90] ChCl/malic acid,[90] and ChCl/polyacrylamide[66] ES solvents can achieve CO_2 permeabilities of 35, 34, 30, and 25 Barrer, respectively, with CO_2/CH_4 selectivities (α) of 57, 55, 51, and 44. In contrast, typical imidazolium-based IL membranes exhibit CO_2 permeabilities ranging from 500 to 1700 Barrer with CO_2/CH_4 selectivities between 12 and 23.[91,92] Furthermore, supported liquid membranes with choline salts/1,2-propanediol ES demonstrate CO_2 permeabilities between 86 and 152 Barrer, with CO_2/N_2 selectivities ranging from 21 to 30. These results align well with the reported selectivities of IL-based supported liquid membranes, such as [emim][Tf_2N] and [C_6mim][Tf_2N], which show selectivities of 23 and 15, respectively.[91,93] Overall, these data indicate that eutectogel membranes are competitive with conventional IL membranes in terms of CO_2 separation performance, positioning them as a greener and more sustainable alternative.

One promising direction for improving the performance of eutectogels in CO_2 separation is the development of mixed matrix membranes. Integrating a third component within eutectogels can significantly enhance the CO_2 separation efficiency. In particular, porous materials such as zeolites, metal−organic frameworks (MOFs), and porous organic polymers (POPs), which are known for their high surface areas and tunable pore structures, can be embedded within the eutectogel matrix to improve gas selectivity and permeability.

Another innovative approach involves the development of facilitated transport membranes (FTMs) by designing eutectogels with specific carriers that can selectively facilitate CO_2 transport. The use of CO_2-philic carriers, such as amine groups within the eutectogel matrix, can significantly enhance CO_2 separation efficiency by improving selective transport mechanisms. For instance, the fabrication of eutectogels with amino acid−based ES such as lysine, arginine, and histidine/betaine systems could be an excellent alternative.[94]

A significant issue is optimizing the mechanical strength and long-term stability of eutectogel membranes, especially under harsh operational conditions such as high pressure and temperature. One approach to enhance structural integrity is the use of dual cross-linking strategies. For example, a combination of covalent and ionic cross-linking can be employed, where covalent bonds provide permanent stability, and ionic interactions offer flexibility and self-healing capabilities. Specifically, introducing a covalent cross-linker like glutaraldehyde alongside ionic cross-linking agents such as divalent metal ions (e.g., Ca^{2+} or Zn^{2+}) could significantly improve the durability and resilience of the membranes.[95,96] Alternatively, incorporating nanomaterials, such as graphene oxide or carbon nanotubes, into eutectogel membranes can further enhance their mechanical strength, thermal stability, and overall gas separation efficiency. Overall, composite materials have shown the potential to strengthen membrane durability and separation performance under various operational conditions.[57,97,98]

Scalability and integration into existing industrial processes are also key challenges. Advances in fabrication techniques, such as 3D printing, could enable the production of complex, high-performance membrane structures at scale.[99]

By focusing on these advanced directions, researchers can address the current limitations and unlock the full potential of

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eutectogel membranes for efficient and sustainable CO_2 separation. Integrating advanced materials, functionalizing eutectogels for enhanced performance, developing innovative membrane configurations, and ensuring the fabrication of sustainable membranes with long-term stability and scalability are key to advancing this promising field.

4. EUTECTOGELS FOR DRUG DELIVERY

The possibility of having a pharmaceutical drug in a liquid state without hazardous solvents has given rise to therapeutic eutectic solvents (THEES) composed of at least one pharmaceutical ingredient.[45] In turn, ES can dissolve hydrophobic or hydrophilic drugs due to their high solubilization capacity and nonaqueous nature, improving the pharmacokinetics of drugs (Figure 3).[100,101]

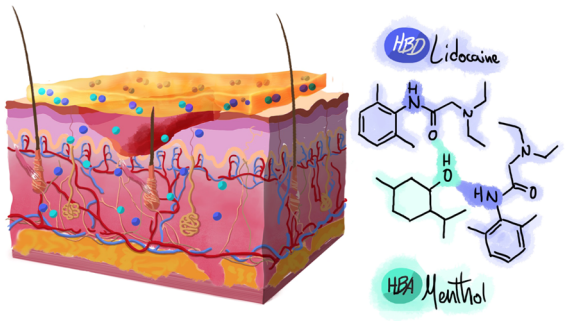

Figure 3. Schematic representation of the concept of eutectogels for drug delivery.

Tailoring the properties of ES by combining diverse components and varying their ratios enables the creation of task-specific solvents responsive to factors such as pH, thermal changes, and radiation.[50,102,103] Furthermore, the low cost, easier preparation, and greener nature of many ES place them as potential alternatives to classic therapeutic ILs.[94] The development of eutectogels containing ES presents an exciting prospect for drug delivery, enabling higher drug-loading capacities. Moreover, incorporating components in the mixture that interact with cells, tissues, and biological membranes increases drug penetration, thereby expanding the scope of noninvasive, drug-targeting, and controlled drug-release treatments. These eutectogels can be obtained by combining LMWGs and ES or by polymerizing monomers uisng ES as the reaction media.[26,50,104] Most of the literature discussing drug delivery via eutectogels focuses on using synthetic polymers, given their good mechanical performance, with PVA being the most employed polymer so far.[105,106] For instance, pH-responsive eutectogels based on PVA and imidazole-based ES have been recently reported for delivering the anticancer drug 5-Fluorouracil.[103] However, from the point of view of biocompatibility, it is necessary to encourage the use of natural polymers to develop eutectogels for drug delivery.

In contrast to synthetic polymers, natural polymers demonstrate advantages in terms of biosafety, accessibility, and modifiability. Additionally, owing to the presence of reactive groups in natural materials, it is feasible to incorporate various functional groups, thereby granting the resultant materials the ability to tailor their physical and chemical attributes.[105,107] For instance, chitosan, collagen, alginate, agarose, starch, and silk fibroin possess excellent bioactive properties, mucoadhesion, fast degradation, and good biocompatibility.[108] Additionally, the gelating properties of these biopolymers enable the formation of suitable soft materials for drug delivery applications.[109−114]

Despite the benefits of natural materials, they often lack sufficient mechanical strength and processability. Hence, viable cross-linking techniques are employed to enhance the strength and stability of biopolymer-based soft materials.[115−117] Among the most used strategies are chemically cross-linking by radical polymerization,[118−120] chemical reaction of functional groups such as OH, COOH, NH_2,[10,121,122] and noncovalent cross-linking through ionic or other interactions.[123,124] Thus, given the wide strategies available to reinforce natural polymers and the tailored properties of ES, scientific efforts need to be focused on these aspects to develop durable soft materials for drug delivery. For instance, Picchio, Calderón et al. developed an elastomeric eutectogel based on choline geranate (CAGE) THEES into a gelatin patch dynamically cross-linked by tannic acid. The patches presented a biocompatible profile and kept the skin permeation properties of CAGE, promoting the dermal delivery of hydrophobic and hydrophilic dyes.[105] Additionally, an innovative eutectogel, comprising gelatin and ChCl/glycerol ES loaded with nanocrystallized curcumin, displayed impressive stretchability and elasticity given by the dynamic interactions between the protein and the ES. It underwent a reversible gel−sol phase transition at a mild temperature (≈50 °C), facilitated 3D printing, and exhibited strong adhesion to mucin. *In vitro*, release studies indicated sustained curcumin delivery for up to 4 weeks, with notably higher drug deposition in excised porcine mucosa.[125] Added to these efforts, Vanoli et al. recently developed a supramolecular hydrophobic eutectogel based on menthol-thymol for the drug delivery of ethosuximide for up to 3 weeks with a dual thermo/pH responsiveness via a diffusion mechanism.[104] Shaw et al. developed a eutectogel based on ChCl/glycerol ES and cellulose loaded with numerous antimicrobial agents and pharmaceuticals such as octenidine dihydrochloride, tetracycline hydrochloride, and fluconazole with successful antimicrobial activity and drug release.[126] Parsana et al. developed conductive supramolecular eutectogel by dissolving pharmaceutically active cetylpyridinium chloride and bromide in ES based on ChCl/formic, oxalic, and citric acid. This eutectogel offers excellent self-healing, injectable, and ionic conductive properties, antimicrobial activity, high encapsulation efficiency, and sustained release of curcumin.[127]

Despite the advancements above, concerted efforts from the scientific community are essential to fully exploit the potential of eutectogels for drug delivery. This requires the use of different biocompatible and biodegradable polymers, formulation of new THEES, and exploration of the solubility curves for new drugs in ES.

For instance, alpha-Lipoic Acid (LA) is a natural molecule recognized for its unique ability to polymerize and depolymerize, making it ideal for creating biodegradable eutectogels. Notably, LA and ChCl can form a polymerizable ES,[128] which, in combination with other eutectic mixtures like glycerol/ChCl and a gelator like gelatin, makes it possible to yield interpenetrated eutectogels. These eutectogels can effectively encapsulate therapeutic agents and offer controlled release profiles that match the polymer's degradation rate. Also, LA exhibits strong adhesiveness to the skin,[129] enhancing its potential in transdermal drug delivery applications. The good skin adhesion ensures prolonged contact and improved drug absorption, making LA-based eutectogels particularly

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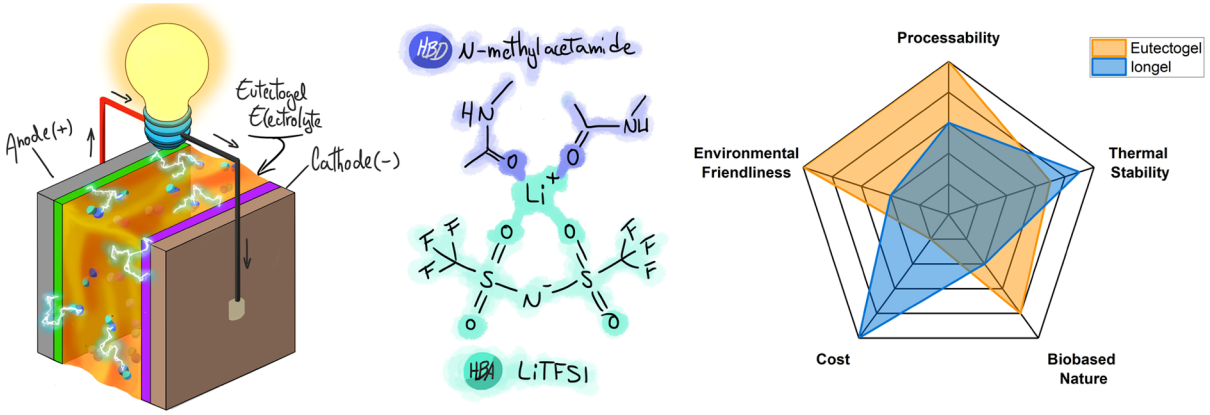

Figure 4. Schematic representation of the concept of eutectogels for drug delivery (left). Radar plots of the properties of Eutectogels and iongels (right). The values (distances from the center) range from 0 to 5, where 5 corresponds to the highest value of a certain property and means certain properties do not apply to this type of soft material.

promising for topical therapies. This combination of biodegradability, biocompatibility, and excellent adhesive properties makes LA-based eutectogels a promising option for advanced drug delivery systems.

Another prime alternative is the use of triamcinolone acetonide, a nonsteroidal anti-inflammatory drug, which offers an alternative treatment for uveitis, an intraocular inflammatory disease. However, the low solubility of the drug continues to limit its incorporation into natural and hydrophilic matrices for subsequent release in the conjunctival sac area.[130,131] Thus, its incorporation into a hydrophobic ES formulation and subsequent preparation of cross-linked eutectogels for sustainable drug release are promising alternatives. Additionally, to enhance drug solubility, triamcinolone can be nanosized by wet milling,[130] allowing its incorporation into a wide range of ES and eutectogel formulations. This treatment can even increase ocular permeation and bioavailability.

The development of eutectogel formulations capable of codelivering chemotherapeutic agents and immunomodulators may also enhance the efficacy of cancer treatment and reduce systemic toxicity. For instance, incorporating both a cytotoxic chemotherapeutic drug, such as doxorubicin and an immunomodulatory agent, such as interleukin-2 or checkpoint inhibitors, into a eutectogel matrix could assess the synergistic effects of codelivery on tumor regression and immune response modulation in preclinical cancer models.[132] Finally, further comprehensive studies on the toxicity effects and environmental stability of THEES, ES, and eutectogels are needed to address some controversial results. Optimization and scale-up of reported processes are also imperative to realize the widespread application of eutectogels in drug delivery.[101]

5. EUTECTOGELS FOR BATTERIES

The versatile properties demonstrated by ES encompass good thermal stability, low volatility, relative nonflammability, electrochemical and chemical stability, effective solvation, and good ionic conductivity.[133] This last feature positions ES as a frontrunner in developing ionic soft materials like eutectogels, presenting a promising avenue for next-generation energy storage technologies. In particular, the wide range of possibilities for developing biobased, nontoxic, and fluorine-free electrolytes for batteries and supercapacitors is interesting. The properties of eutectogels can be finely tailored by adjusting the chemical composition of the ES and gelator, manipulating their proportions, and modifying the type of interactions, along with the degree of cross-linking.[65] Notably, the ratio of ES to gelator plays a pivotal role in determining the ionic conductivity of eutectogels, with higher ES content often correlating with enhanced conductivity levels.[134,135] Eutectogels, with their flexibility and versatility, emerge as ideal candidates for battery applications, offering self-healing capabilities and stretchability akin to traditional solid materials.[136,137] Compared to iongels, eutectogels have exhibited similar properties in terms of ionic conductivity, self-healing capabilities, and mechanical performance but benefiting from a lower cost, greener nature, and straightforward preparation of the ES electrolyte.[138] However, since ES are mixtures of compounds, some of which may be volatile, the thermal stability or volatility of the resulting ionic eutectogels could be compromised compared to ILs gels.[18] This limitation, however, can be effectively addressed by carefully selecting the components of the eutectic system. For instance, betaine is an exceptional HBA that interacts strongly with HBDs. Its strong interaction leads to the formation of ES with a significant negative deviation from thermodynamic ideality, thereby enhancing the stability and reducing the volatility of the resulting eutectogel.[139]

A difficult task will be to develop eutectogels without fluorinated compounds, which show the high electrochemical stability required for lithium or sodium metal batteries. Figure 4 depicts a qualitative comparison between eutectogels and iongels as solid electrolytes in energy storage applications. It is worth mentioning that the current library of eutectogels for batteries is broadening,[134,140,141] although this realm is still in its infancy.

In this perspective, we will focus on lithium-ion batteries, given their dominance in the commercial battery market as next-generation high-energy-density solutions.[142] In this sense, the limitations on the electrochemical and thermal stability of conventional ES, particularly those based on organic salts like ChCl and urea, have limited their utilization as electrolytes for lithium batteries. Efforts to enhance the electrochemical stability of eutectogels have led to promising developments, such as those utilizing lithium salts as HBA to form ES.

Pioneering studies by Joos et al. demonstrated that eutectogels based on bis(trifluoromethane)sulfonimide lithium/*N*-methylacetamide ES condensed using tetraethylorthosilicateor embedded into a polymer network of 4-acryloylmor-

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pholine and ethylene glycol dimethacrylate show wide electrochemical windows and good cyclability.[135,143] Concerning some disadvantages of these materials, such as weight loss at temperatures above 80 °C and some flammability, Hou et al. developed a water-in-eutectogel imbibing a microporous dry polymer with a ternary lithium salt:acetamide:H_2O ES an exhibiting high ionic conductivity, wide electrochemical stability window, nonflammability, and decomposition temperatures above 120 °C.[137]

Despite the thermal stability, next-generation energy storage devices should be green, soft, stretchable, and self-healable.[144] As demonstrated by Xu et al., the natural polymer cellulose combined with lithium salt-based ES can form a eutectogel with retardant flammability, capacity retention rates of 50 cycles at 0.2 C under 100 °C, and excellent ionic conductivity of 2.04×10^{-3} S cm^{-1} at 30 °C.[19] A very recent work presents a eutectogel electrolyte composed of a mixture of lithium salts and succinonitril to form a eutectic electrolyte with fluoroethylene carbonate as an additive that then was encapsulated within a polymer matrix.[145] This eutectogel shows a significant improvement in thermal stability with weight loss at 150 °C up to 17%, nonflammable nature, and capacity retentions of 72.5% and 87.7% after 1500 and 100 cycles at high charging voltages of 4.45 and 4.6 V, respectively. Self-healing, thermal stability, and rechargeable batteries are needed to overcome challenges related to recycling. In this sense, lithium salt-based-ES, in combination with acrylate monomers and fluoroethylene carbonate as an additive, can develop self-healing polymers with high stability, safety, and cyclability.[140]

An interesting approach is to develop biobased eutectogels using ES compositions based on lithium salts and natural organic acids, such as citric acid or tartaric acid, to improve electrolyte stability and conductivity.[146−148]

Despite progress, challenges related to recycling processes, environmental impacts, and the establishment of recyclability still need to be addressed. A deeper exploration of eco-friendly and biodegradable ES is required for their implementation as an alternative to conventional ES in eutectogel formation. One possibility to minimize the environmental impact is to synthesize eutectogels using natural ES based on terpenes, sugars, or organic acids extracted from renewable biomass sources that can dissolve lithium-based salts.[149] A comprehensive assessment of ES after their use is essential to promote sustainable practices and minimize the environmental footprint of eutectogels as solid-state electrolytes and beyond.

6. EUTECTOZYMES: EUTECTOGELS IN BIOCATALYSIS

Biocatalytic reactions are typically conducted in a water-based environment, which can present limitations related to the poor solubility of hydrophobic substrates due to the high polarity of the medium. For this reason, alternative reaction media, including organic solvents, supercritical fluids, and ILs, have been explored. However, adopting these solvents is often curtailed by their toxicity, low compatibility with the enzyme, and high cost, opening new opportunities for ES technology.[150,151] In the last years, ES has proven effective in improving substrate solubility and stabilizing various enzymes, spanning hydrolases, oxidoreductases, peroxidases, transferases, and lyases, facilitating both single and multistep transformations involving organocatalyst/enzyme and metal/enzyme combinations.[152]

The strategic immobilization of enzymes within suitable support media represents an attractive avenue for enhancing biocatalyst stability, reusability, and ease of separation. This approach also allows for the confinement of enzymes with cofactors or chemical catalysts in defined volumes, offering unique opportunities for developing synergistic combinations.[153] Traditional methods of protein immobilization typically involve covalent attachment to heterogeneous supporting materials or noncovalent entrapment within porous matrices, creating an engineered environment that shields the enzyme from denaturation and poisoning. Such entrapment alters the immediate surroundings of the protein by constraining the enzyme within the solvent held within the matrix.

Enzymes have been successfully entrapped in water-free supramolecular structures, as Imam et al.[116] recently demonstrated. They entrapped a lipase in ILs supramolecular gels, resulting in biocatalytic materials with exceptional shelf-stability and high recyclability. Alternatively, Kumar et al.[17] have proposed the utilization of eutectogels to entrap enzymes, introducing a new category of materials called "eutectozymes" (Figure 5). Using sustainable solvents, these "eutectozymes,"

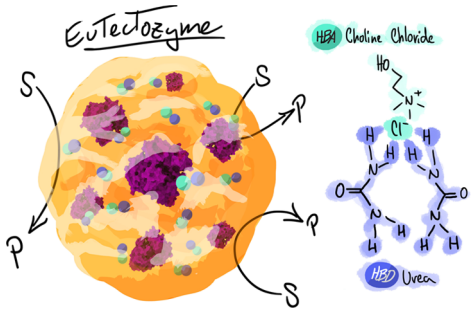

Figure 5. Schematic representation of the concept of enzyme immobilization within eutectogels denoted as "eutectozyme" and the different biocatalytic reactions that could be carried out in this soft material.

could offer the benefits of solid supports, such as enhanced biocatalyst stability and the potential for recycling and continuous operation.[17]

Immobilizing enzymes within eutectogels is an entirely unexplored concept, unlike other soft materials such as hydrogels, which have been widely investigated for this goal.[154] Thus, combining enzymes with ES within gel networks offers opportunities to create functional materials with unique properties. For instance, hybrid protein/eutectogels could come with unique synergistic properties when combined, for example, with the therapeutic activity of THEES. Also, ES can be combined with enzymatic reactions that are valuable in the biomedical space, while the eutectic medium boosts the biocatalyst performance. Another interesting case may be the immobilization of catalase in eutectogels containing ES based on either fatty acids with antimicrobial activity or polyphenols with anti-inflammatory properties, which could be highly attractive as therapeutic patches for diabetic chronic wound treatment. In these functional materials, catalase would provide oxygen to the wound microenvironment, as it plays a crucial role in the healing process by promoting cell proliferation and protecting them from hypoxia-related damage.[155] Additionally, combining glucose oxidase (GOx) with ES based on anticancer drugs would improve the tumor permeability, solubility, and diffusion rate as they remain in a permanent liquid state.[156] In this sense, GOx is another biomedically relevant enzyme that

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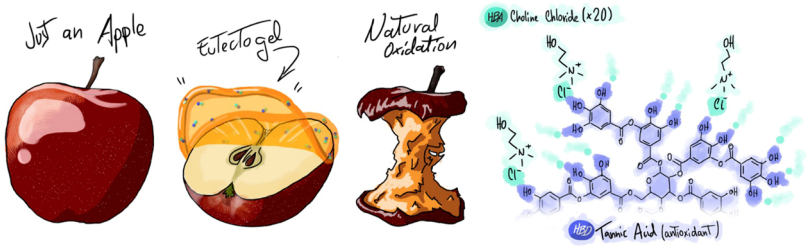

Figure 6. Schematic representation of the concept of active eutectogels for food packaging applications.

has recently gained significant interest in starvation therapy for cancer treatment.[157] This therapy is based on the catalytic depletion of intracellular glucose, cutting off the nutrition source of cancer cells and consequently inhibiting their proliferation.[158] Alongside these developments, a recent strategy has been employed in which eutectogels were synthesized by free radical polymerization of acrylamide in the presence of an α-helical peptide cross-linker in ChCl: urea or ChCl: ethylene glycol ES.[159] Acrylamide, the α-helical peptide, and a photoinitiator were dissolved in the ES and then exposed to UV light, forming an ultrastrong eutectogel. The incorporation of various inorganic elements, such as metal nanoparticles/clusters, MXenes, perovskites, and metal–organic frameworks (MOFs), alongside enzymes, presents an innovative pathway for utilization in biocatalysis, sensing technologies, wearable or implantable devices, flexible materials for soft robotics, and artificial skins.[160,161] A careful selection of ES, guided by a comprehensive understanding of their structural intricacies and their effects on biomacromolecules and inorganic components, represents a transformative shift in biohybrid soft materials, opening up vast possibilities. This approach offers potential benefits for protein engineering, especially for enzymes reliant on cofactors, as the proximity of responsive metals can enhance their activity. Moreover, it could streamline one-pot chemoenzymatic reactions that require the collaboration of both artificial and natural catalysts.

In conclusion, while ES are extensively explored in biocatalysis, combining enzymes with eutectogels presents an exciting approach to delve into the design of sustainable and green catalytic materials. This approach spans from the macro to the nanoscale and offers improved properties, potentially unlocking unlimited opportunities for technological innovations.

7. EUTECTOGELS FOR FOOD PACKAGING

Currently, petrochemical polymers are the predominant materials used in food packaging. This dominance stems from historical factors, cost-effectiveness, and effective mechanical and barrier properties. However, these polymers are nonbiodegradable, raising significant global environmental concerns in the short and long-term.[162] As a result, there is mounting pressure on the food industry to explore alternative packaging materials, focusing on those derived from natural, renewable sources, or environmentally sustainable biopolymers. However, the food packaging industry demands the incorporation of compounds or additives that prolong the shelf life of products while offering resistance, barrier properties, and nontoxicity to biodegradable materials. These packaging materials are referred to as "active packaging systems." Among the various types of active packaging, antimicrobial packaging stands out as a highly innovative and promising development in the past decade derived from the fact that the growth of fungus or bacteria on the surface of food is one of the factors that have the greatest influence on the loss of quality of the products and their end of useful life.[163]

Within the world of ES, natural ES (NAES) are composed of natural components that can offer antioxidant and antimicrobial properties, moisture regulation, and cross-linking properties, plus the nontoxicity and high biodegradability of the obtained material. The common mixtures used to form NAES include ChCl with organic acids, polyphenols, polyalcohols, and sugars.[164−167] Importantly, the vast number of primary metabolites available from plants, their active properties as antioxidants or antimicrobials, and the possibility of using high amounts of these active compounds in a liquid state at room temperature open up opportunities for innovative packaging designs. For instance, in a recent work, soy protein-based films were developed with high concentrations of NAES (up to 200 wt %) based on ChCl and tannic or citric acids, showcasing excellent antimicrobial and antioxidant activity as well as cross-linking and plasticizing effects.[11] Moreover, their combination with natural polymers such as gelatin, cellulose, chitosan, and xanthan gum allows the development of natural eutectogels with excellent mechanical properties.[168−172] These natural eutectogels could be used to replace traditional petroleum-based plastics, providing a more sustainable and eco-friendly option (Figure 6).[168]

The use of ternary NAES, a mixture of three or more compounds in a particular molar ratio, is an interesting approach to include two or more active compounds in the same solvent. This approach allows the development of *"all-in-one"* natural eutectogels that have antioxidant and antimicrobial properties. For instance, citric acid demonstrates exceptional antimicrobial activity, whereas tannic acid has excellent antioxidant performance. Thus, the ternary NAES formed by these compounds could offer both features. Most advances in eutectic technology for food packaging have been carried out using hydrophilic NAESs, whereas hydrophobic ES are a less explored subclass.[173] A criterion for classifying ES as hydrophobic is the formation of a two-phase system when mixed with water.[174] The use of hydrophobic NAES could lead to natural eutectogels with low water uptake resistance, low water vapor transmission rate, and antimicrobial and antioxidant activities. A representative example of hydrophobic NAES for food packaging is the study by Wang et al. based on chitosan/gelatin films with up to 15 wt % of thymol/caprylic acid NAES displaying good antibacterial activity and water vapor transmission rate.[175] Thymol, menthol, eugenol, carvacrol, and fatty acids are excellent hydrophobic compounds to consider when fabricating NAES. In fact, mixtures of thymol and fatty acids usually show stronger hydrophobic properties compared to quaternary ammonium-based ESs.[176] Long and medium-chain fatty acids have superior properties

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over many short-chain acids, such as good chemical stability, nontoxicity, antioxidant, and antimicrobial activity, whereas thymol, carvacrol, eugenol, and menthol act as HBA and have remarkable antifungal, and antioxidant activity.[177−179] Additionally, hydrophobic NAES, such as those composed of thymol, menthol, or other natural terpenes, and fatty acids, can form hydrophobic soft materials by photopolymerization of acrylic monomers.[180,181] These hydrophobic soft materials exhibit excellent stability and low water uptake, a feature needed to preserve water-sensitive food such as coffee, flour, and dehydrated soups, among others. However, the development of hydrophobic eutectogels involves the use of synthetic acrylic monomers. Therefore, it is necessary to exploit hydrophobic natural polymers such as zein protein or copal and damar gums, which are hydrophobic resins of the plants *Bursera bipinnata* and *Shorea wiesneri*, respectively.[182] An interesting challenge is presented when hydrophobic NAES are combined with hydrophilic natural gelators such as proteins or polysaccharides. One simple strategy that helps to combine both components is high-speed homogenization to create a stable oil-in-water emulsion, as is usually assayed for oil incorporation in protein aqueous dispersions.[122]

Natural eutectogels hold significant promise as sustainable and effective solutions for enhancing food packaging capabilities and reducing environmental impact. Challenges such as scalability, cost-effectiveness, and regulatory approval should be addressed before natural eutectogels can be widely adopted in the food packaging industry. Further research is needed to fully understand the long-term stability and safety of natural eutectogel packaging materials in contact with various types of food.

8. CONCLUSIONS AND OUTLOOK

Eutectogels represent a promising frontier for addressing several contemporary challenges across diverse fields. In the scope of CO_2 separation, eutectogel membranes offer an alternative to traditional methods by leveraging their cost-effectiveness, selectivity, and high CO_2 permeability. The promising results from recent studies suggest that further refinement of ES components, especially the selection of HBA and HBD, can significantly enhance CO_2 solubility and separation efficiency. Specific advancements could include the design of novel ES formulations with lower viscosities to enhance mass transfer rates and the development of advanced cross-linking methods to increase mechanical strength and operational stability. For example, the use of hybrid ES formulations combining low-viscosity HBA with CO_2-philic HBD-like amines can significantly improve CO_2 solubility and separation efficiency, thereby making these materials more suitable for industrial CO_2 capture applications.

In drug delivery, eutectogels have emerged as versatile materials capable of achieving high drug-loading capacities and controlled release mechanisms for drug delivery. The integration of natural polymers with ES can create biocompatible and biodegradable delivery systems, potentially transforming therapeutic practices. Furthermore, the incorporation of components with additional properties (enhancing penetration through biological membranes, recognition of the therapeutic targets, etc.) would allow the preparation of multifunctional materials with relatively simple formulations. For instance, integrating biodegradable polymers such as gelatin with polymerizable ES based on LA could improve the long-term stability and biodegradability of the drug delivery systems. Researchers should focus on developing robust synthetic strategies that enhance the mechanical properties of these delivery systems. For instance, optimizing the molecular weight of polymers and tailoring gelation conditions could improve the controlled release profiles, leading to more effective therapeutic outcomes. Furthermore, a detailed investigation into drug solubility in different ES formulations is crucial to maximize efficacy and reduce potential toxicity.

In energy storage, eutectogels are promising candidates for use as solid-state electrolytes in next-generation batteries, particularly due to their excellent ionic conductivity and flexibility. Recent developments in enhancing the thermal stability and nonflammability of eutectogels are crucial for their application in lithium-ion batteries. Future research should focus on the integration of conductive nanomaterials, such as graphene or carbon nanotubes, to enhance both ionic conductivity and mechanical properties. Furthermore, exploring recyclable ES formulations based on renewable feedstocks will ensure the sustainability of these materials for large-scale battery applications.

In biocatalysis, eutectogels offer a novel platform for immobilization, enhancing enzyme stability and reusability while facilitating complex catalytic processes. The unique properties of ES can improve substrate solubility and enzyme activity, paving the way for more efficient and sustainable biocatalytic systems. This is a completely unexplored topic, and some researchers have already foreseen the emergence of hybrid soft materials called eutectozymes.[17]

For food packaging, eutectogels based on NAES represent a sustainable alternative to traditional petrochemical-based plastics. When integrated with biopolymers, these materials can exhibit antimicrobial and antioxidant properties, helping to extend food shelf life while being environmentally friendly. Future efforts should focus on developing eutectogels with ternary NAES formulations to obtain soft materials with *all-in-one* functionalities, such as antioxidant and antimicrobial properties and enhanced oxygen and moisture barriers. Moreover, research aimed at optimizing these formulations to meet industrial and regulatory standards will be key to their widespread adoption in commercial food packaging applications.

Overall, the versatility and tunable properties of eutectogels hold immense potential for innovation in various industries. Continued interdisciplinary research and collaboration are essential to overcome the current limitations, optimize the material properties, and fully harness the benefits of eutectogels for practical applications. The future of eutectogels is auspicious, with potential breakthroughs that could significantly affect environmental sustainability, healthcare, energy storage, biocatalysis, and food packaging.

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