

Catalytic applications of deep eutectic solvents

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(DOI: 10.30495/IJC.2023.1974539.1981)

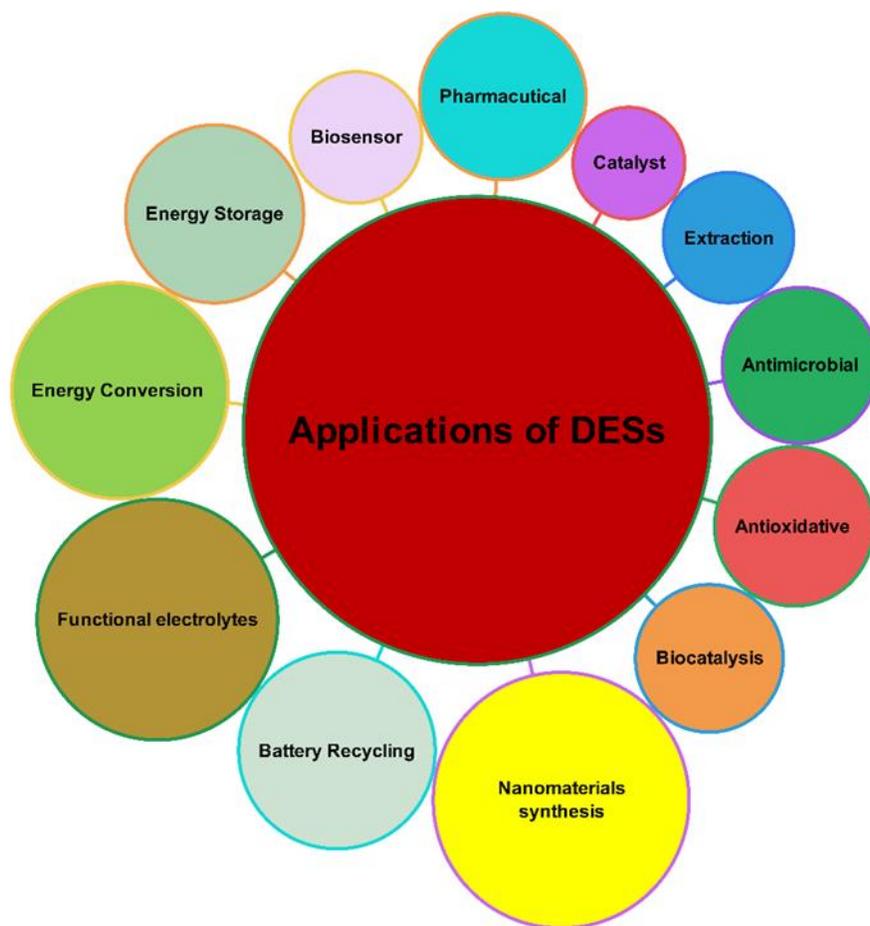


This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

In 2003 Abbott et al. reported a new generation of ionic liquid (IL) entitled deep eutectic solvents (DESs), a new class of solvents. DESs have two or three components with a large depression of melting points [1]. These ingredients involve a variety of ionic and neutral species and have the role of either hydrogen bond acceptors or hydrogen bond donors, which play the role of Lewis or Bronsted acids and bases [2]. Recyclability, low vapor pressure, and low toxicity are important properties of deep eutectic solvents. These Eco-friendly properties of deep eutectic solvents have attracted researchers' attention [2, 3]. Bio-oil and biofuel productions [4-7], catalysis [8-12], separation processes [16, 17], and extraction [13-15] are some applications of DESs. Furthermore, they can be obtained easily without purification [3, 18]. Uniquely, the probability of tailoring the solvent is a significant property of DESs [2]. Due to these properties, DESs have greater application than ILs [19], which are already great in this consideration. Changing the molar ratio of the components or replacing a component with another one brings desired property for related DES or even by adding a certain amount of a cosolvent

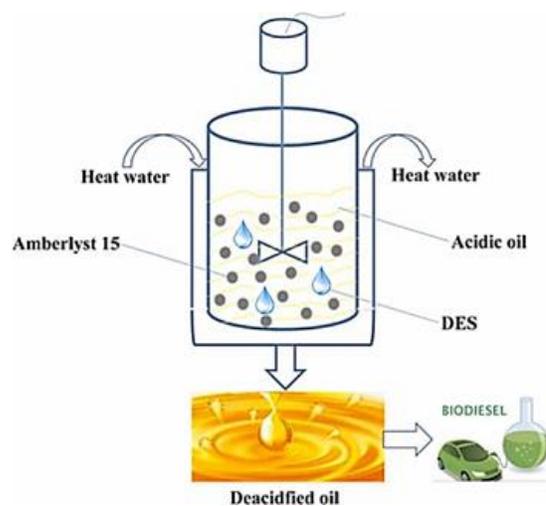
[20-22] such as water [23-26]. Due to the van der Waals and electrostatic forces [29] and extensive hydrogen bonding (H-bonding) networks between species [27, 28], most DESs have high viscosities [2]. By mixing DES with water, their high viscosity can reduce [23-26]. The cosolvent can affect the essential and desirable properties of DES [25]. For this reason, care must be taken when we dilute a DES with a cosolvent. Most of the distinctive properties of DESs are due to some specific underlying intermolecular interactions, like H-bonding, which is important in this matter. For example, the notable decrease in the melting point of a typical DES is supposed to arise from the charge transition between components, from the halide anion of hydrogen bond acceptors to the hydrogen bond donors through H-bonds [22, 26, 30]. It has been made clear that by strengthening the H-bonds between hydrogen bond acceptors and hydrogen bond donors, the melting points further decrease [1]. Depending on the composition of DESs and their molar ratio, DESs may reduce thermal stability [31-33]. Some of the applications of DESs are shown in Scheme 1. In this spotlight, I am going to highlight the catalytic applications of DESs.



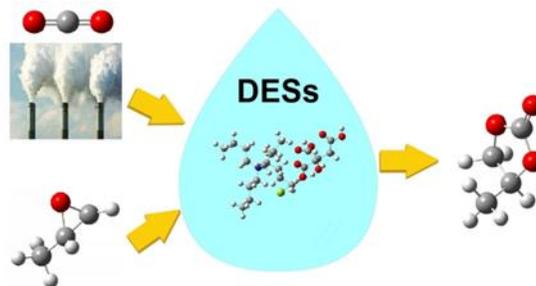
Scheme 1. A few DESs applications

Abstracts

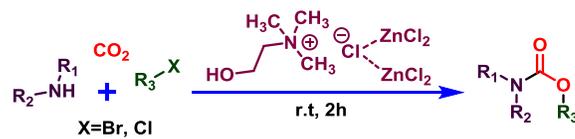
(A) DES has a crucial role in the deacidification of acidic oil. Deacidification is a critical step in alkali catalyzed transesterification of acidic oil for biodiesel production. In this work, Weidong Lu and colleagues investigated the optimization of the process variables into the mechanisms of DES assistance for the deacidification of acidic oil catalyzed by Amberlyst 15 [34].



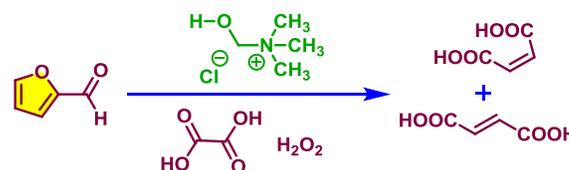
(B) In this work, Zixian Wang and colleagues used TBAB/CA DESs as catalysts for the coupling reaction between CO₂ and epoxides, which showed excellent catalytic activity and good substrate suitability under mild reaction conditions. The synergistic catalytic effect between the intramolecular hydrogen bond and the flexible nucleophilic Br⁻ anion may decrease the energy barrier of the ring-opening process and accelerate the CO₂ cycloaddition reaction [35].



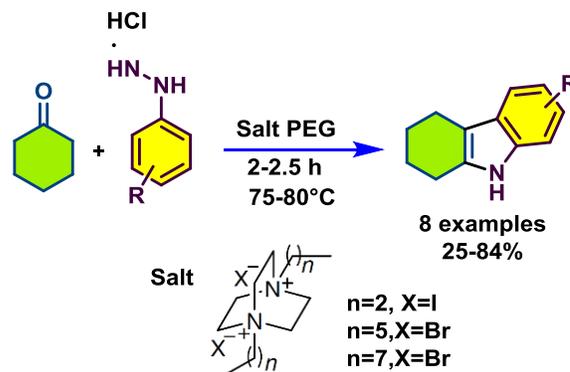
(C) In 2019, Dindarloo and Majnooni synthesized an eco-friendly catalyst based on DES. They devised a simple synthesis route for carbamates through a three-component coupling of amines, alkyl halides, and CO₂. This is the first report of using DES as a solvent/catalyst system that catalyzed carbamates formation from amines, alkyl halides, and carbon dioxide [36].



(D) Herein, an easy procedure was investigated to oxidize furfural to both maleic acid and fumaric acid in DES as a green solvent Lifeng Yan and co-workers. The DES contains choline chloride and oxalic acid, which oxalic acid can play two roles as both an acidic catalyst and the main content of the solvent. According to the paper, it proved that the conversion percentage of furfural could reach 100%. In comparison, the maleic and fumaric acid yield reached 95.7% under moderate reaction temperature (50 °C), which provides an efficient and green route to synthesizing valuable monomers from furfural [37].

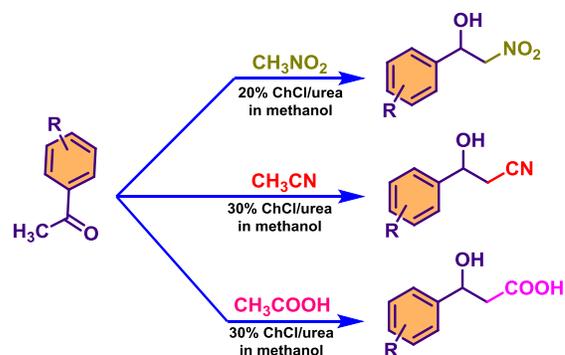


(E) In 2017, Imran Malik and co-workers reported some unconventional DESs composed of 1,4-diaz-abicyclo [2.2.2] octane and polyethylene glycols-based salts. The prepared DESs work as solvents and catalysts in the Fischer indole synthesis. The route to get these novel DESs was *N*-alkylation of 1,4-diaz-abicyclo [2.2.2] octane using alkyl halides and subsequent mixing with hydrogen bond donors [38].

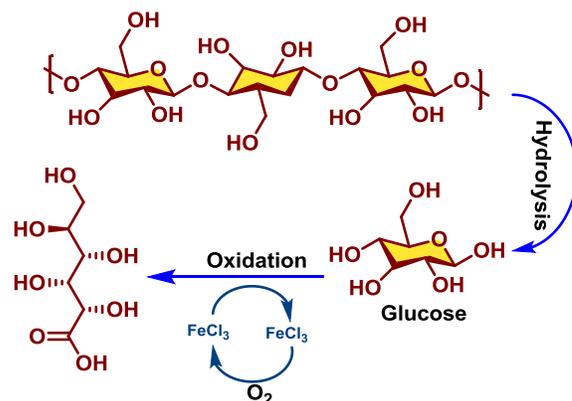


PEG: Polyethylene glycols of various molar masses

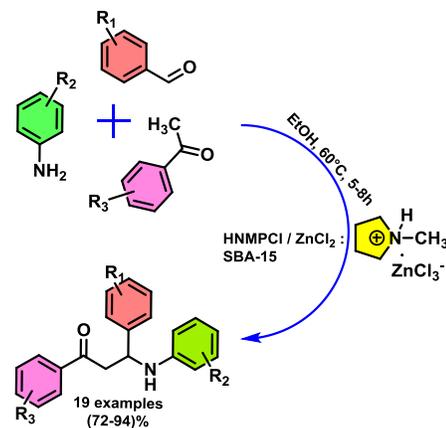
(F) In 2012, Shankarling and co-workers explored the versatility and effectiveness of DES as a catalyst in three different carbon-carbon bond formation reactions. More to the point, a productive synthetic protocol employing ChCl/urea DES as a catalyst could rapidly synthesize β -hydroxy functionalized derivatives [39].



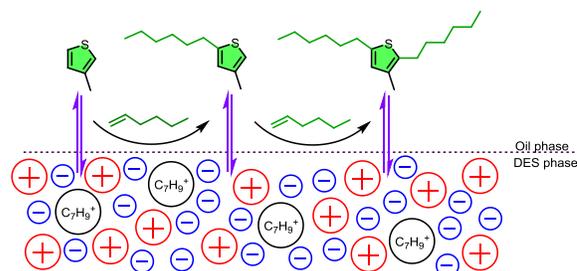
(G) Liu and co-workers reported a chemo-selective and highly efficient cellulose conversion to gluconic acid, which uses $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /ethylene glycol (EG) deep eutectic solvent in 2018. According to the paper, an acidic deep eutectic solvent hydrolyses cellulose into glucose that, in the presence of air, can be oxidized by FeCl_3 [40].



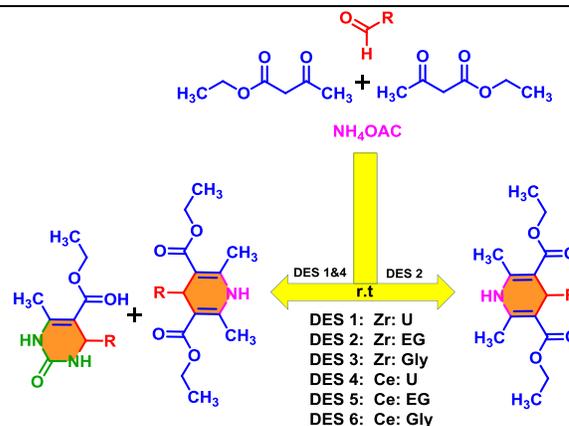
(H) Najmedin Azizi and co-workers described an immobilized DES on mesoporous silica as a heterogeneous ionic catalyst for the Mannich reaction of aromatic amines, aromatic aldehydes, and acetophenone. The separable hybrid catalyst, HNMPCl/ZnCl₂/SBA-15, has been developed for the one-pot three-component Mannich reaction, which can catalyze the reaction efficiently in ethanol [41].



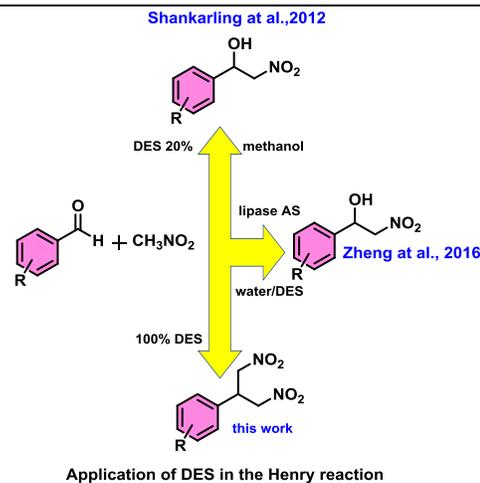
(I) DESs prepared using acetamide and AlCl_3 or urea show brilliant catalytic performance for the OATS (olefin alkylation thiophenic sulfur) in 3-MT (3-methyl thiophene) model oil and gasoline during 40 min at 50 °C. Based on a report by Tang and his colleagues in 2015, the addition of benzene and toluene enhances the conversion of thiophenic compounds and reduces the conversion of olefin [42].



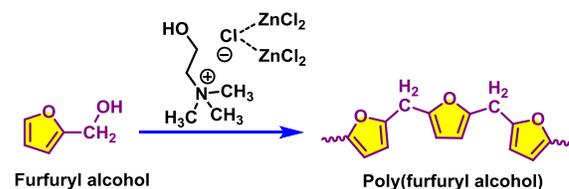
(J) Synthesis of symmetric dihydro pyridine systems from a three components reaction between ethyl acetoacetate, aldehyde and ammonium acetate, which catalyzed with a deep eutectic solvent reported by Shaibuna and Sreekumar in 2021. The present article reports the adaptability of six DESs for Hantzsch dihydropyridine synthesis at room temperature. According to the paper, DES 2 was found to be a catalyst for the Hantzsch reaction with excellent recyclability [43].



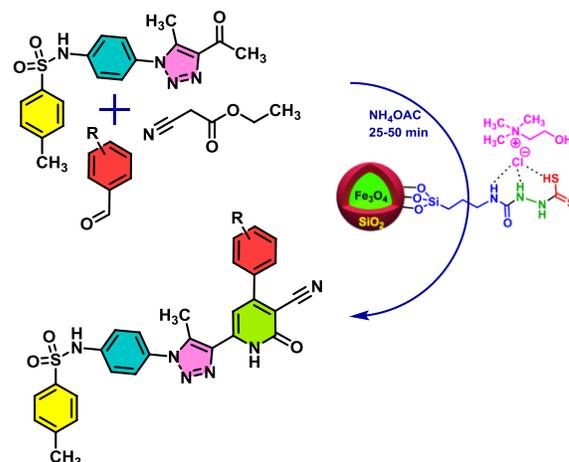
(K) Another example of the catalytic application of DES (choline chloride/urea) is their application in the Henry reaction, which was performed using microwave heating and acted as both the catalyst and solvent for the reaction. In 2020, Greta Colombo Dugoni and co-workers reported a straightforward synthesis of symmetric 1,3-dinitropropanes with excellent selectivity and good yields of the tandem Henry reaction/Michael addition under DES-MW conditions [44].



(L) In 2022, Cao and co-workers reported a pathway for the polymerization of furfuryl alcohol into poly (furfuryl alcohol) using a DES system that can efficiently catalyze furfuryl alcohol polymerization without using any external solvent and catalyst. The DES was prepared by mixing choline chloride (ChCl) and zinc chloride (ZnCl_2) [45].



(M) In the Zolfigol group, $\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-urea-dithiocarbamic acid/Ch-Cl}$ has been synthesized as a heterogeneous catalyst. This catalyst was applied as recoverable and naturally sustainable for synthesizing innovative hybrid pyridones containing sulfonamide and triazole pieces [46].



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