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Deep eutectic solvents as environment-friendly solvents for separation processes in the oil and gas industry

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Abstract. Oil and gas are still the primary energy source in the world, despite the advancements in renewable energy. Many researchers showed chemical enhanced oil recovery, particularly surfactant is the most efficient method in many reservoirs. But most of these projects were not only commercially successful (due to high cost), but also involve environmental issues. Recently, Deep Eutectic Solvents (DESs) were discovered as a cheaper and greener alternative to conventional surfactants. DESs are cost-effective, easy to prepare, non-toxic, recyclable, biodegradable and environmental-friendly. Due to these advantages, DESs have found application in different fields including the oil and gas industry. The main applications of DESs in the oil and gas industry are separation processes such as dearomatization, desulfurization, purification of biodiesel and CO_2 capture. In this paper, the performance of DESs in these processes was reviewed as a new environmentally friendly method. The study introduces a way forward for current challenges with environmental sustainability.

Introduction to Deep Eutectic Solvents

Search for green chemical solvents is always in progress. Abbot et al. introduced DESs and defined them as new-generation sustainable solvents and potential alternatives to ionic liquids (ILs) and conventional organic solvents [1]. Fundamental properties of DESs are similar to ILs such as density, viscosity, conductivity, surface tension, high thermal stability and negligible volatility. DESs are cheaper, easy to prepare and more environmentally friendly compared to ILs. They are recyclable, biodegradable, non-corrosive and non-flammable [2].

The eutectic system is defined as “Eutectic system is a mixture of chemical compounds or elements that exhibit a single chemical composition that freezes at a lower temperature than any other composition” [3]. The eutectic point is the intersection of eutectic composition and eutectic temperature. DES is consisting a minimum of two green low-cost components that can form a eutectic mixture, having the melting point lower than its components [1].

Synthesis of DES

DESs are made by a special mixing of some of the hydrogen bond acceptors (HBAs) such as quaternary ammonium salts and a hydrogen-bond donor (HBD) at a specific ratio (molar) [4]. The mechanism by which a DES is formed is not complicated. The HBD interacts with the anion of the HBA (salt) and as a result, the effective size will be increased, at the same time, it reduces interactions of the anion with the involved cation. As a result, the produced DES melting point will be reduced [5, 6]. In general, DESs are characterized by a large depression of the freezing point and by being liquids at temperatures maximum at 150 °C. However, the majority are liquid somewhere between room temperature (20 °C) and as high as 70 °C.

The most studied DES constituents are choline chloride and urea which was first introduced by Abbott and co-workers in 2003. For choline chloride, the melting temperature is 302°C and for

urea, the point is known to be 133°C. When the two materials were mixed at a 1:2 molar ratio of choline chloride: urea, a liquid eutectic mixture was formed. Choline chloride is considered green and it doesn't have any harmful effects [7]. It is mostly used as a vitamin for animals. Urea (carbamide) is well-known agricultural fertilizer. Since the constituents are not harmful when mixed resulting DES is also totally green [8].

Heating and grinding methods are two main types of methods that are used for the preparation of DES [9]. The most commonly used one is the heating method which is based on mixing and heating the compounds at 100 °C with stirring constantly until clear liquid is achieved. In the grinding method, compounds are mixed at room temperature and ground with a pestle in a mortar until a homogeneous liquid is formed.

DESs are produced without chemical reactions and need catalysts. While producing ILs involve raw material reacting chemically and by-products that will form impurities and as a result, they require extra purification work [10]. Unlike traditional ILs, the preparation of DESs is simple just by mixing and heating the compounds under stirring without the requirement of a catalyst. Moreover, overall mass efficiency and zero-emission during synthesis are achieved. As a result, all the involved salt and HBD are converted to DES, which as stated earlier, is completely environment-friendly as there are no unwanted by-products, including any vapours [11].

DESs are cheap due to their simple synthesis and cheap components. No purification is required and there is no waste production. DESs have high boiling points and low vapour pressures and most of their components are non-toxic and biodegradable [12, 13]. All these advantages increased interest in DESs as greener alternatives for ILs. Gurkan et al. reported the number of publications and citations for DES by 2019, as shown in figure 1 [14]. We can see that research in this area increases significantly in recent years.

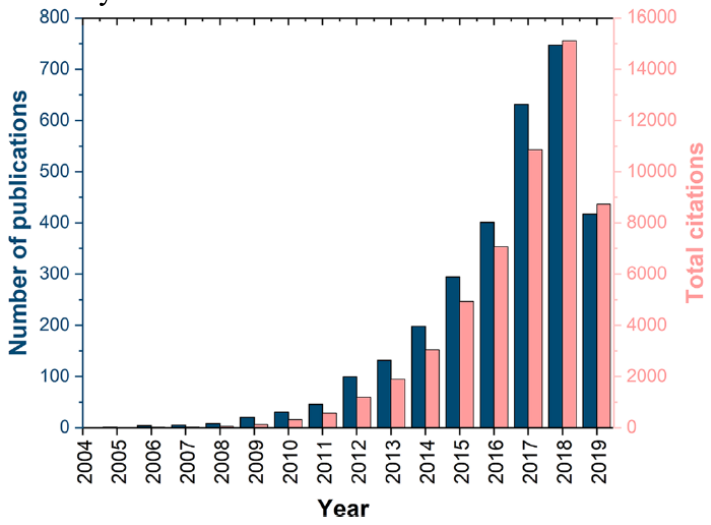

Fig. 1. Total Publications and Citations for DES [14]

Types of DES

DESs are mainly classified into four main types. Smith et al. showed the classification of DESs using the formula generally shown as $Cat^{+}X^{-}zY$, in which the Cat^{+} is a cation, X^{-} is an anion and also Y is Brønsted or Lewis acid. Moreover, z shows the Y molecule numbers that would interact with the anion) [15]. Table 1 shows DESs formed from a general MClx in the first part followed by quaternary ammonium salts.

Table1. A Types of DESs [15]

Types	General formula	Terms	Example
Type I	$Cat^+X^- + zMCl_x$	M = Zn, In, Sn, Al, Fe	$ChCl + ZnCl_2$
Type II	$Cat^+X^- + zMCl_x.yH_2O$	M = Cr, Ni, Cu, Fe, Co	$ChCl + CoCl_2.6H_2O$
Type III	$Cat^+X^- + zRZ$	Z = OH, COOH, $CONH_2$	ChCl + Urea
Type IV	$MCl_x + zRZ$	M = Zn, Al and Z = OH, $CONH_2$	$ZnCl_2$ + Urea

Type I: Composed of organic salts and metal salts.
Type II: Composed of organic salts and metal salt hydrate.
Type III: Composed of organic salts and HBD. This is the most common type.
Type IV: Composed of metal salts and HBD.

Properties of DESs

Freezing Point.

The low freezing point of DESs is one of the important properties which makes them unique. As mentioned earlier Abbot et al. showed the formation of a unique solvent with 12 °C as the freezing point, which is considerably lower than its components when mixed at a 1:2 molar ratio of choline chloride: urea [1]. Moreover, Kareem et al. presented a solvent formation with a melting point of – 66 °C from a 1:2 molar ratio of choline chloride: ethylene glycol [16].

Many factors can contribute towards the freezing point of the DESs such as the nature of the organic salt, the choice of HBD, the organic salt/HBD molar ratio and the anion of the organic salt. No correlation was concluded between the melting points of the individual components and the freezing point of the synthesized eutectic mixture [4].

Viscosity.

DESs have high viscosity due to the hydrogen bonding between components which reduces the mobility of compounds [5]. Van der Waals or electrostatic forces might cause high viscosity as well.

The DES viscosity is mainly affected by the individual component properties such as temperature, water content, and salt/HBD molar ratio [4]. Florindo et al. showed that by adding water to the system, the viscosity decreases drastically around 10-30 times [9]. At 25 °C, by hydrating ChCl: urea alongside 6 wt% of water, viscosity was reduced 13 times compared to the viscosity of dry ChCl: urea [17].

Du et al. studied the effect of water presence (2.5–20 wt%) on the three most common choline chloride-based DESs, namely (1) Reline (ChCl: urea), (2) Ethaline (ChCl: ethylene glycol) and (3) Glycerine (ChCl: glycerol) as shown in figure 2 [17].

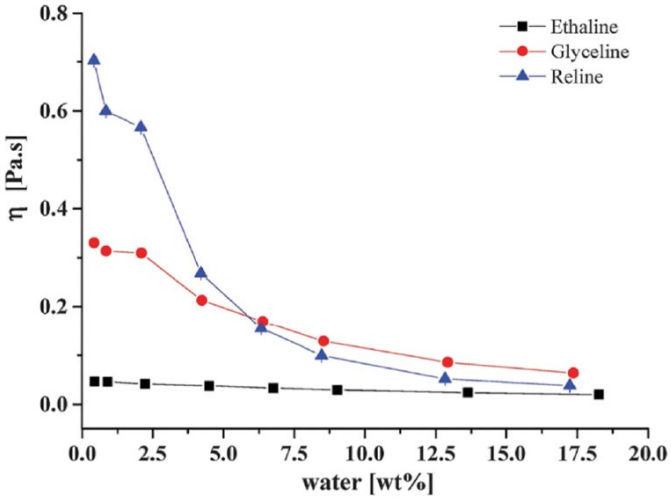

Fig. 2. Effect of Water Content on Viscosity for ChCl-based DESs at 20 °C [17]

It was observed that with the water content increasing, the viscosity decreased in all of the examined liquids. However, the decrease is not steady. The effect of the percentage of water on the viscosity of Reline was more than the other two liquids. Whereas, there is a small effect for Ethaline.

Abbott et al. showed the effect of ChCl concentration and temperature on the viscosity of the ChCl: glycerol mixture as shown in figure 3 [18]. The viscosity of pure glycerol (without ChCl) is around 1200 cP. It can be observed from the figure viscosity decreases by increasing temperature and ChCl concentration. A significant viscosity reduction of glycerol by the addition of ChCl was explained as due to the partial break of the strong hydrogen bond network of glycerol.

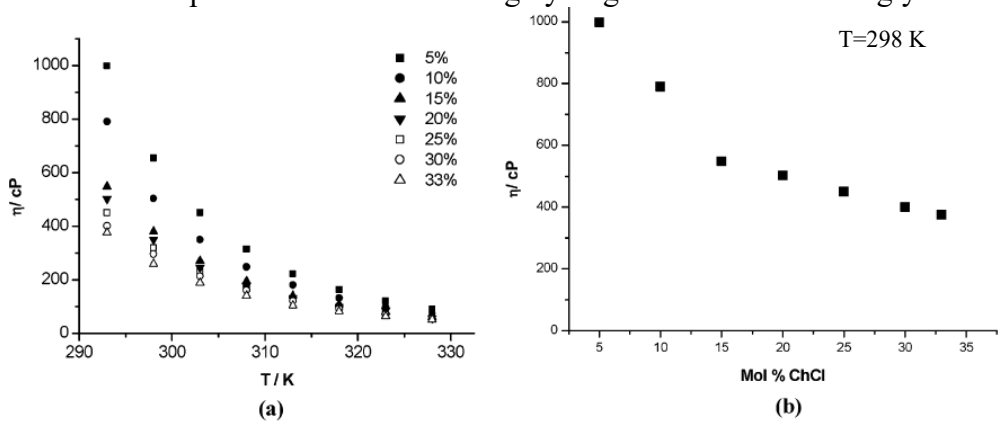

Fig. 3. Effect of Temperature (a) and ChCl concentration (a and b) on Viscosity [18]

Density.

Several studies were performed for the measurement of densities of DESs as a function of temperature [9, 12, 18]. Results showed that density decreases with increasing temperature which is the same behaviour as most of the liquid phase materials. The range of density of common DESs varies between 1.04-1.63 g/cm^3 at 25 °C and the salt/HBD molar ratio has a significant effect [4].

Conductivity.

Most of DESs have low ionic conductivities (lower than 2 mS cm^{-1} at 20 °C) due to their relatively high viscosity [4]. The viscosity of DES decreases with increasing temperature which increases ionic conductivity. Moreover, the ionic conductivity of DES increases with increasing water content due to the decrease in viscosity.

Applications of DESs for Efficient Separation Processes in the Oil and Gas Industry

Since the introduction of DES at beginning of the 21st century, their applications in areas are widening due to their advantages. The main advantages of DESs compared to ILs can be summarized as lower cost, non-toxicity, easy preparation, biodegradability and elimination of the purification step. Even though the main research area of DESs is chemistry [19], interest in other fields is also increasing including the oil and gas industry. The main applications of DESs are in the fields of extraction and separation processes, catalytic reactions and electroplating, material preparation, hydrometallurgy, biomass treatment and pharmaceutical applications [20, 21]. Important separation applications of DESs in oil and gas fields can be presented below:

Dearomatization

The separation of aromatic from aliphatic compounds is important to improve fuel properties and reduce environmental impacts. However, this is not an easy task due to very close boiling points and the formation of azeotropes. There are several processes such as liquid-liquid extraction (LLE), azeotropic distillation, extractive distillation and membrane processes. The most widely used method in industry is liquid-liquid extraction due to its low cost, simple operation and low energy consumption. In this method selection of extractants is vital. Organic solvents are the most commonly used chemicals but due to their volatility and toxicity, it is important to find novel solvents that will allow green and efficient separation [21].

ILs have been studied as an alternative to organic solvents by several researchers. Improved separation performance was achieved with most of the ILs compared to organic solvents. But due to the drawbacks of ILs as discussed before DESs started to be studied as an alternative to ILs for the removal of aromatics and to improve efficiency [22].

Kareem and his team investigated the separation of toluene and heptane with DES composed of tetra-butyl phosphonium-bromide as a salt and ethylene glycol or sulfolane as HBDs [23]. Tests were performed at different temperatures and different salt: HBD molar ratios. Results showed satisfactory performance of DESs for extracting aromatics and they exhibited higher selectivity at low concentrations of toluene compared to high ones.

Mulyono et al. performed the separation of different materials including ethylbenzene, toluene, benzene, and m-xylene (BTEX) aromatics from n-octane using a DES (tetrabutylammonium bromide + sulfolane) [24]. From the results benzene>toluene>m-xylene>ethylbenzene was the order of extraction performance on aromatics. Moreover, it was proven that the selective extraction of BTEX aromatics was possible from a mixture of aromatic and aliphatic compounds using DES.

Hou et al. investigated the separation of toluene from the toluene and n-hexane (or cyclohexane) mixtures using DES consisting of tetra-butyl phosphonium bromide (TBPB) and levulinic acid (LA) at different temperatures and molar ratios [25]. The optimal condition was achieved with a 6:1 molar ratio of levulinic acid: TBPB and a molar ratio of 6.4:1 of the DES: toluene at 20 °C. By distillation at 100 °C toluene in DES was completely recovered and DES was reused. It was concluded that the separation by DESs showed significance in terms of extraction rate and high selectivity.

Gouveia et al. evaluated the separation of toluene from n-heptane with a liquid-liquid extraction method using DESs [26]. DESs were based on various HBAs (cholinium chloride, tetrabutylammonium chloride, and benzyl-cholinium chloride) and levulinic acid as HBD with the 1:2 mole ratio of HBA: HBD. Improvement of the distribution coefficient led to the introduction of a more hydrophobic HBA and higher selectivity achieved by playing with the aromaticity of the DES.

Larriba et al. tested the extraction of aromatic hydrocarbons from reformer and pyrolysis gasoline using choline chloride-based DES [27]. In this study six choline chloride-based DESs (levulinic acid, malonic acid, ethylene glycol, phenylacetic acid, glycerol, and urea as HBDs) were

tested. From the results, DES formed by choline chloride and levulinic acid (1:3) was selected as the most promising one.

Feng et al. studied the effective separation of aromatic hydrocarbons by pyridine-based DES [21]. The pyridine-based DESs were consisting of N-ethyl-pyridinium bromide and two HBDs (N-formyl morpholine and levulinic acid). By liquid-liquid extraction method, two ternary systems, toluene + n-heptane + DES and benzene + cyclohexane + DES were studied. N-formyl morpholine DES showed better performance in terms of separation compared to levulinic acid. The best separation for both DESs was at room temperature (20 °C) and a relatively low percentage of the aromatic concentration.

Desulfurization

Sulphur dioxide (SO_2) is a harmful gas to human health and the ecosystem. It is produced by the combustion of sulfur-containing fuels such as coal, oil or diesel. Exposure to SO_2 causes several health problems such as asthma, neurological disorders, wheezing and irritation of the skin are only some of them [28, 29]. Moreover, SO_2 damages the ecosystem as a result of acid rain. Due to these reasons, numerous regulations have been imposed to reduce SO_2 emissions. Maximum Sulphur content that is allowed in the fuel is one of these regulations. In recent years more strict policies are being taken [30].

Considering these circumstances, Sulphur removal from sour crudes is an important task to meet fuel standards. There are three Sulphur removal methods: Solvent extraction, catalytic hydro-desulphurization (HDS) and adsorption on molecular sieves. HDS has been the commonly used method to remove sulfur from crude oil but it is unable to remove polycyclic organic sulphides [30]. Due to these reasons and also due to the simplicity of the process, low energy consumption research on solvent extraction techniques is increasing. In this method, solvents are used to remove Sulphur compounds from the hydrocarbon stream based on the liquid-liquid extraction principle. Solvent selection is a key factor. Conventional solvents are alkanol amines. Past few years ILs have been widely researched. However, due to raised concerns about ILs such as toxicity and non-biodegradability of some ILs, in recent years DESs gained more attention as an alternative.

Li et al. reported the first paper on DESs as a solvent for desulfurization [31]. Desulfurization of fuels was carried out with ammonium-based DESs. Successful desulfurization of fuels was achieved from these DESs. Tetrabutylammonium chloride: polyethene glycol showed the optimum condition with an extraction efficiency of 82.83% for one cycle which is much higher than traditional solvents and ILs. Moreover amount of Sulphur in fuels decreased below 8.5 ppm.

Using $FeCl_3$-based DES, Gano et al. studied the desulfurization of simulated fuel and commercial diesel [32]. As a sulfur compound, dibenzothiophene and thiophene were present in the simulated fuel. Results showed 64% of extraction efficiency for dibenzothiophene and 44% for thiophene in a single-stage extraction. Due to the satisfactory results obtained for simulated fuel, the solvents were used for the desulfurization of real commercial diesel. Total sulfur removal from the diesel was 32%. Additionally, it was concluded also DESs could be regenerated and used repetitively without a significant decrease in their sulfur removal ability.

Makos and Boczkaj successfully applied DES (ChCl: phenol) for the desulfurization of model liquid fuel which contains thiophene, benzothiophene and dibenzothiophene [33]. The best conditions were the 1:4 mole ratio of ChCl: phenol, 2.5:1 volume ratio of DES: Fuel, 40 °C of temperature and 40 minutes of extraction time. In optimum conditions, the removal efficiency was 91.5% for thiophene, 95.4% for benzothiophene and 99.2% for dibenzothiophene in a one-step process. After three stages this value was 99.99%.

Purification of Biodiesel

Compared to fossil diesel, biodiesel is considered clean and renewable fuel which is less toxic and produces less amount of greenhouse gases [34]. After production biodiesel should be purified to pass standards. The glycerol is an undesirable by-product and must be removed before the biodiesel can be used as a fuel. It increases the viscosity of fuel and damages the injection system of diesel engines [15]. Glycerol is highly polar and unlikely to biodiesel. Liquid-liquid phase decantation is a common method for the separation of glycerol but a non-negligible amount remains and extra treatments are required [5].

Abbott et al. studied the removal of glycerol from biodiesel in two ways [35]. Initially, they added pure quaternary ammonium salt to glycerol-containing biodiesel to form a eutectic mixture with glycerol. This approach was not successful. It was stated this might be due to enthalpy formation. After that, they prepared DESs (ammonium salts: glycerol) and demonstrated the successful extraction of excess glycerol from biodiesel. For extraction of glycerol from the biodiesel the most effective molar ratio was 1:1 of glycerol: salt. Among the studied salts best results were achieved with choline chloride. The efficiency of glycerol removal was up to 99%. After studying the recovery of ammonium salts, it was observed that 25% of choline chloride could be recovered.

Shahbaz et al. presented the separation of glycerol from palm oil-based biodiesel using different combinations of DESs (ChCl: ethylene glycol and ChCl:2,2,2-trifluracetamide) [36]. All DESs showed successful results which removed all free glycerol with an efficiency of >99%. Moreover, Shahbaz et al. reported the removal of residual catalyst (KOH) from palm oil-based biodiesel using DESs.

Niawanti et al. performed a purification of biodiesel using choline chloride-based DESs. DES was a mixture of a 1:2 molar ratio of choline chloride: ethylene glycol. Best conditions were achieved when the molar ratio of crude biodiesel: DES was 1:4 with an efficiency of 96.60 %. The authors concluded that based on their study DES can be used for the purification of biodiesel from non-edible raw materials [37].

Salic et al. evaluated biodiesel purification in micro extractors using the water washing method and also using seven different DESs that are based on ChCl: glycerol and ChCl: ethylene glycol mixtures [38]. Three different sizes of micro extractors were used for both methods. Results from both processes compared to each other. DESs showed advantages over the water washing method such as higher efficiency, a lower amount of solvent usage, and less waste to be treated at the end of the process. It was possible to separate purified diesel and DES at the end of the micro extractor and recirculate DES. Figure 4 shows a graphical illustration of processes.

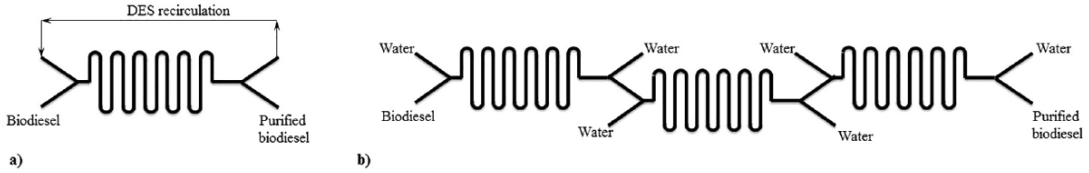

Figure 4. Glycerol Removal Using (a) DES and (b) Water Washing (Source: Salic et al., 2020)

CO_2 Capture

Global warming is one of the biggest issues in the world, especially in recent years. Great efforts are focused on reducing global warming. The emission of CO_2 gas is one of the major causes of global warming. Several technologies have been studied that are free of CO_2 emissions. But most of them are not yet at the stage of large-scale implementation. On the other hand, a large number of techniques and research are being conducted for CO_2 capture. Fossil fuels are the main cause of

CO_2 emissions which is the most important energy source. Hence, reducing CO_2 emissions from industry is essential [39, 40].

CO_2 capture using aqueous ethanolamine solutions such as monoethanolamine (MEA) and diethanolamine (DEA), has been introduced and studied broadly [41]. Even though studies showed efficient CO_2 capture, there are several drawbacks reported that need to be taken into account. The main drawbacks include corrosion problems due to the corrosive property of ethanolamine solutions, high cost due to high energy consumption, degradation, high solvent volatility and toxicity. Due to these drawbacks, ILs were proposed [42] but they have several limitations also as discussed in previous parts such as high cost and not being ecologically advantageous. DESs emerged recently as being free from most of these disadvantages [43].

As a first quantitative study, Li et al. presented DESs as a potential CO_2-capturing method [44]. Solubility of CO_2 in ChCl: urea DES was measured at different temperatures, pressures and molar ratios. Results showed solubility increases with increasing pressure and decreases with increasing temperature. Different molar ratios didn't have a significant impact on solubility.

Mirza et al. performed experiments and thermodynamic modelling on three different DESs to analyze the solubility of CO_2 at different temperatures and pressures [45]. Three different DESs were reline (ChCl:urea with 1:2 molar ratio), ethaline (ChCl:ethylene glycol with 1:2 molar ratio) and malinine (ChCl:malic acid:ethylene glycol with 1.3:1:2.2 molar ratio). The experimental study observed Henry's constants were between the ranges of 3.7-6.1 MPa. Thermodynamic modelling was used to correlate experimental data and results showed excellent agreement with a 1.6% deviation.

Ali et al. examined different types of DESs for the feasibility of the CO_2-capturing process [46]. The best performance was seen from methyl triphenylphosphonium bromide: monoethanolamine DES with a molar ratio of 1:6. Moreover, it was shown that the energy requirement with MEA-based DESs is lower than the energy requirement with the classical MEA process. However, a large solvent/feed ratio was required for all investigated DESs.

Zhang et al. also investigated CO_2 capture by DESs [47]. Results showed excellent CO_2 absorption capacity of DESs up to 1.00 mol CO_2/mol DES, and by changing the mole ratio of HBA and HBD, the absorption process could be adjusted. Moreover, high thermal stability and excellent recyclability were observed in the studied DESs.

Conclusion

In this paper, the applications of DESs in separation processes were reviewed. The DESs showed great potential in DES as a new-class green solvent for the oil and gas industry. The study proved the effectiveness of DES not only in improving oil recovery, but also in CO_2 capture, purification of biodiesel, desulfurization, and dearomatization. This study also introduces a way forward for current challenges with environmental sustainability. The new class solvents are not only green but also exhibit better performance than current similar solvents with added economical benefits.

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