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Deep Eutectic Solvents as the New Norm for Oil and Gas Industry: A Mini Review

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ABSTRACT

As the new type of green solvents, Deep eutectic solvents (DESs) might be the key to a better future. This mini review presents a brief discussion on the applications of DESs especially in oil and gas sector published in the past half a decade. Several reviews made on applications of DESs in different sectors are also highlighted for readers' perusal. It is hoped that this work may encourage the engineers and problem solvers in the industry to opt for greener option in their applications.

Keywords: *Petroleum industry, green application, gas hydrate*

1. INTRODUCTION

The Covid-19 pandemic has made the human population more aware of the rising environmental issues. With the energy demand drastically dropped, the petroleum industry has been hugely affected. However, as soon as the pandemic is over, the oil and gas sector will be back in demand again. It is a major responsibility to seek eco-friendly solutions to be implemented in the exploration, transmission and processing of oil and gas. The common issues in the petroleum industry are hydrates, waxing, asphaltenes, slugging, naphthenates, scales, corrosion, and emulsions, which often need different chemical solvents to be considered. Unfortunately, the chemicals are usually toxic in nature and the alternatives are rarely found [1,2].

Deep eutectic solvents (DESs), a relatively new type of green solvents, have been earning some attention in the world of science and engineering many areas of science and technology. The DESs may offer a solution for the various issues in the petroleum industry. This mini review offers an insight to the history of DES, the current applications of DES in the industry and discuss the possibility of DES to be implemented as a green solution for the major issue of petroleum industry, the gas hydrates formation. It is inevitable that this mini review leaves out some important papers and does not cover all the existing works on DESs.

2. DEEP EUTECTIC SOLVENTS

The word "eutectic" originated from a Greek term meaning low melting and applies to either an alloy or liquid medium. Generally, a eutectic system is a mixture of components having the lowest melting point through virtue of specific proportions. Without covalent or ionic bonds, these components interact merely through intermolecular forces [3]. Liu et. al. [3] have noted that the history of DESs starts in the year of 1918 with the observance of the eutectic mixture of sodium amide and potassium amide formation. The exponential growth in the number of researches started in 1980s and in the year 2003 DES was introduced as the analogue of ionic liquids (ILs) [4]. According to Tomé et. al. [5] who have tabulated their findings after reviewing multiple works on the preparation methods of DESs, most of the DESs can be prepared through agitation method which is by direct mixing, stirring and heating at respective conditions.

As a subclass of ionic liquids, DESs display comparable characteristics. DES are easy to be synthesised due to lower cost of the raw materials and are relatively cheaper. DESs are also less toxic and often biodegradable [6]. However, it must be noted that DESs and ILs are significantly different. Eutectic mixture of Lewis or Brønsted acids/bases forms DESs, which has various of anionic and/or cationic species. However, ILs are primarily composed of one type of discrete anion and cation [7]. Commonly, DESs are derived from two or more salts as the hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs) [8,9]. There are four types of DES that can be formed [5,7] as tabulated in Table 1.

Table 1 Types of deep eutectic solvents

Type	Combination
I	quaternary ammonium salt + metal chloride
II	quaternary ammonium salt + metal chloride hydrate
III	quaternary ammonium salt + hydrogen bond donor
IV	metal chloride hydrate + hydrogen bond donor

Despite the presence of different types of DESs, type III DESs are the most explored category as the availability of wide range of hydrogen bond donors indicates the adaptability of this class of DESs [7].

The preparation of DES is simple by the mixing of HBD and HBA at a specific temperature in of two ways, (1) when the HBD and HBA are mixed, the lower melting point constituent begins to melt and then the remaining compound which has a high melting point is put into the liquid and the mixtures are melted collectively, and (2) when both constituents are mixed and melt together, since the first work of Abbot et al. 2003 [10].

For example, the solid beginning material of ChCl and Urea were heated at 1:2 proportional to acquire a blend that was liquid at ambient temperature, numerous DES prepared, as studied in [11][12]. Figure 1 represents components in DES and how it interacts or make the bond with one another during the formation of DES molecule.

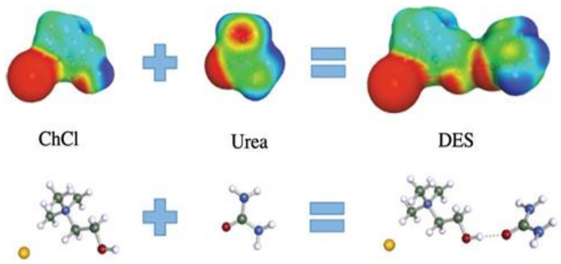

Figure 1 Chemical structure type III DES [13]

Appreciating the works of previous researchers, it is discovered that DESs have been implemented in many industries. As Shishov et. al.[6] list out, DESs are applicable in many areas including nanotechnology, biodiesel synthesis, biocatalysis, electrochemistry, extraction and separation, synthesis of polymers and related materials. The interesting characteristics of DESs as noticed by several experts enable it to be potential candidate for green solution in separation and extraction technology, biotechnology, environmental engineering, absorption & adsorption and even in treating wastewater [14–20].

3. APPLICATIONS IN THE OIL AND GAS SECTOR

Despite the numerous findings on versality of DESs, the green solvent has been mostly overlooked by oil and gas enthusiasts. The authors of this mini review found very limited works done on DESs in the past five years. It is undeniable that oil and gas or well known as fossil fuels account for 81% of the global energy mix currently [21]. However, many issues must be overcome before the fossil fuels are made available for our daily use. The removal of harmful impurities and the flow assurance for the smooth transmission of the fuel are the major operations that should be considered. In terms of removing the impurities, sulphur removal, mercury removal, dearomatization, and CO_2 capture play a significant role. Through this mini review, the authors highlight the significant potential of DESs in this sector.

In a work done on sulphur clean fuel, Lima et. al. [21] claim that all 16 DESs synthesized could successfully remove Thiophene and Dibenzothiophene from the samples with extraction efficiency ranging from 6% to 85%. The work by Li et. al. [22] proves that DES-M (M denotes the malonic acid used as the dicarboxylic acid for the synthesis) can achieve 94.14% removal of sulphur from FCC gasoline in one cycle. DES can really be comparable green alternative for the desulphurization process [21–29]. A comprehensive review by Chandran et. al. [30] listing the various successful DESs for desulphurization, claim that DESs selection influences the removal efficiency and the component of organosulphur compounds being extracted. Almost 100% sulphur removal can be achieved through multistage extraction depicting deep desulphurization to less than 10 ppm of sulphur conforming to Euro 5 standard.

Besides removal of sulphur, DESs composed using either betaine or choline chloride as the HBA and either glycol, levulinic acid or urea as the HBD have shown mercury removal efficiencies to be more than 80% for solvent: feed ratios of 1:1 and 2:1 [31]. Work done by Chen et. al. [32] shows ternary hydrosulphonyl-based deep eutectic solvent can achieve 99.91% mercury removal under optimized conditions.

The review done by Warrag et al. [25] lists the potential usage of DESs in dearomatization, desulphurization and CO_2 removal/capture. Extraction of sub-quality natural gas usually lead to relatively high amounts of impurities, such as CO_2, which have to be removed prior to usage [25,33]. There are two CO_2 absorption methods namely, physical, and chemical absorption. However, conventional solvents used for physical absorption have various environmental issues that need be replaced.

In a simulation done by Haghbakhsh and Raeissi [33], using conventional Selexol and DESs Reline and Glyceline, the resulting methane stream had purities of 89.1%, 90.1%, and 79.6% respectively. Many such experimental researchers have found DESs to be highly affective green solvent for CO_2 capture [15,17,34]. In addition, DESs are also very capable in the section of Enhanced Oil Recovery [35–37].

Study done by Mohsenzadeh et. al. [36] shown that 12% additional recovery was observed compared to primary or secondary steam flooding, when the steam flooding incorporated with undiluted DESs injection and 2-fold diluted DESs injections. DES really has a huge potential to be a green alternative for a lot of processes in the oil and gas industry.

The mechanism of dearomatization, desulphurization and CO_2 removal are all based on the hydrogen bond inter-action of DESs with the atoms need to be removed. The hydrogen bonding property, charge delocalization that occurs due to hydrogen bonding are major factors affecting the process of impurities removal. Figures 2, 3, and 4 show simple examples of mechanism involved in DES based dearomatization, desulphurization and CO_2 removal respectively. Besides the removal of impurities and enhanced oil recovery, DESs also plays a role in the field of flow assurance. Flow assurance covers a lot of issues including the dangerous formation of gas hydrates and corrosion in oil and gas pipelines [38–40]. The detailed corrosivity study by Ullah et al.[34] on CO_2 saturated DES system and CO_2 saturated MEA system had corrosion rate of 0.027 mm/year and 0.54 mm/year respectively. This proves that the DESs of cholinium chloride and levulinic acid are good candidates for corrosion inhibition in the fuel pipelines. However, very few research works have been done DESs as gas hydrates inhibitors.

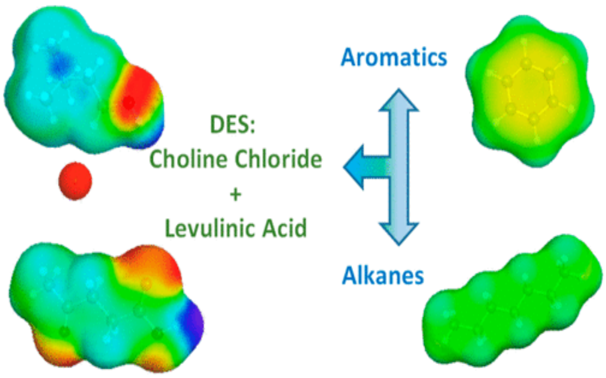

Figure 2 Dearomatization mechanism of DES[41]

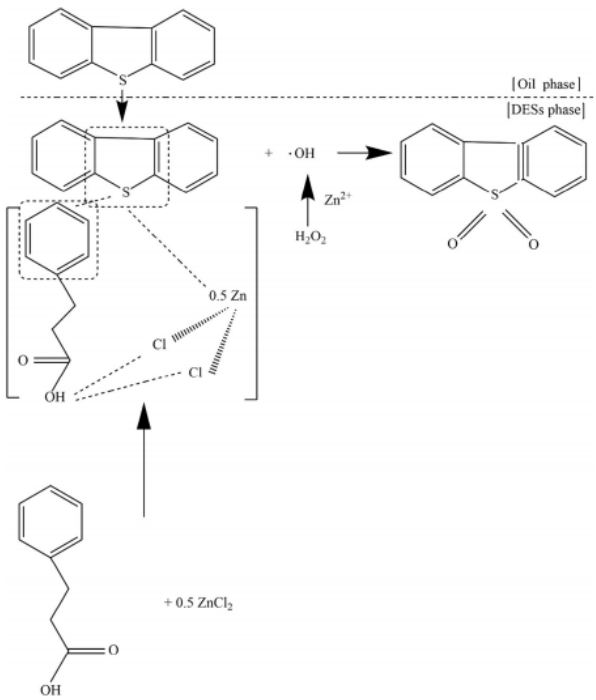

Figure 3 Desulphurisation mechanism of DES[30]

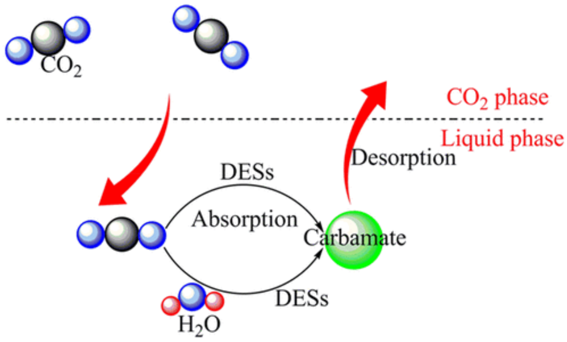

Figure 4 CO_2 removal mechanism of DES[42]

4. DEEP EUTECTIC SOLVENTS AS HYDRATE INHIBITORS

Gas hydrates are often referred to as solid inclusion compounds made up of a network of water molecule cages which act as "host" that could trap light hydrocarbon as "guest" molecule. The risk of gas hydrate formation conditions is highly prevalent and poses a major operational and safety challenge [2,43]. Although many methods are handled to prevent the hydrate formation, the chemical inhibition method is the most prevalent [44].

The conventional method of preventing gas hydrates issues in the pipelines is to implement thermodynamic hydrate inhibitors (THIs) injection. The THIs works by moving hydrate equilibrium conditions to higher pressure and lower temperature regions [45–49]. DESs have great potential to be efficient THIs because they have functional groups capable of forming hydrogen bonds with water, have high biodegradability and low toxicity, besides exhibiting negligible vapor pressure [8,9].

The nature shown by choline chloride, propanedioic acid, 3-phenylpropionic acid, itaconic acid and 3-mercaptopropionic acid based DESs, as potential shale inhibitors in water-based drilling fluids is an extra evidence of the DESs to be efficient THIs[14]. In the work related to dehydration of natural gas by Aissaoui et. al. [50], DESs based on choline chloride displayed significant absorption of H_2O from natural gas down to the concentrations specified for pipelines to avoid hydrate formation. In an one of its kind data by Lee et al [51], DES of choline chloride and urea has been tested on methane hydrates, and the observed gas hydrate inhibition was in the order of ChCl > DES > urea. Although the DES could not beat the performance of pure ChCl, it shows the potential of DES to be a thermodynamic gas hydrate inhibitor.

As DESs are generally formed by mixing HBD and HBA, there is a significant margin to be exploited in making the greener gas hydrate inhibitors. Many substances of tested to be potential gas hydrate inhibitors but having either biodegradability or performance issues. However, mixing compounds to make DESs may be a beneficial act. For example, mixture of choline chloride and urea displays an added advantage as each single component in that can produce a DES.

Even the highly efficient Tetraethyl Ammonium Bromide can be reacted with Glycerol or Glycols to form the applicable DESs. There are many chemicals that can be utilized to be DES based gas hydrate inhibitors with the same approach. The vast choices available for synthesizing efficient DESs based gas hydrates inhibitors have been really taken for granted. It is the authors' hope to see more research being done in the fuel industry towards greener processes after the Covid-19 pandemic subsides.

5. CONCLUSION

Greater number of researchers are looking into greener alternatives as the awareness towards the environmental issues increases. After several comparative studies, DESs are superior in many aspects including non-toxicity, and low-cost preparation opportunity. DESs have been successful in many areas including metal processing, extraction, biotransformations and organic synthesis. DESs hold a great potential to be the green solutions to many issues in the industry. This mini review briefly looks into the various applications of DESs in the oil and gas industries, from the removal of impurities, enhanced oil recovery to the prevention of flow assurance issues. Variety of mixtures ending up being DESs are suggested based on their previous performance. Many more detailed attempts are required to enhance the utilizations of DESs in the industry.

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