

POLITECNICO DI TORINO

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Master of Science in Petroleum Engineering

EVALUATING DEEP EUTECTIC SOLVENT AS A NOVEL ENHANCED OIL RECOVERY METHOD



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ABSTRACT

In recent times, Ionic liquids (ILs) gained more attention as an alternative to surfactants in Enhanced Oil Recovery (EOR). But they are considered expensive for industrial application and some types of them are toxic and not biodegradable. Newly, Deep Eutectic Solvents (DESs) were introduced as cheaper and greener alternatives to ILs. Therefore, it is important to perform a comprehensive study to analyze their performance. In this paper, the performances of DESs were evaluated as a novel EOR method. Based on an accurate literature revision and analysis, numerous studied DESs were analyzed considering their effects on different EOR mechanisms such as stable emulsion formation, IFT reduction between oil and DES/brine solution, wettability alteration, oil recovery improvement, and formation damage. After analysis, their performances were compared with each other. In order to perform a comparison at similar conditions, they were divided into groups based on experimental conditions, core sample properties, and crude oil types. The economic aspect was also analyzed by considering the cost of other chemical EOR methods.

The injection of DES solutions showed a significant amount of oil recovery. Total oil recovery was even higher when steam flooding performed after the DES injection. Analyses indicated that all studied DESs had good potential to change wettability towards the less oil-wet conditions. This was the main mechanism for oil recovery improvement. Only malonic acid (MA) based DESs showed limited emulsion formation with oil, others didn't have emulsification capacity. For heavy oil reservoirs, an increase of IFT rather than decrease was observed. For light and medium oil reservoirs, IFT reduction was seen. Moreover, DESs didn't show any formation damage. Comparing the performance of DESs by considering additional oil recovery due to DES injection after brine flooding, Choline Chloride (ChCl):Glycerol (1:2) showed the best performance with an additional oil recovery of up to 30 %OOIP. Cost assessment showed this method will have a lower cost compared to other chemical methods due to low DES cost and simple preparation. But detailed techno-economic analysis should be performed considering capital and other expenditures. Even though DESs showed promising results as a novel EOR method, there are a few experimental and simulation studies present. Therefore, it is still at the early stage of development.

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LIST OF ABBREVIATIONS

ASP	Alkali-Surfactant-Polymer
BTEX	Benzene, Toluene, Ethylbenzene, and Xylene
ChCl	Choline Chloride
CSS	Cyclic Steam Stimulation
DEA	Diethanol Amine
DES	Deep Eutectic Solvent
DI	Deionized
EG	Ethylene Glycol
EOR	Enhanced Oil Recovery
ES-SAGD	Expanding Solvent Steam Assisted Gravity Drainage
FCM	First Contact Miscible
HBA	Hydrogen Bond Acceptor
HBD	Hydrogen Bond Donor
IL	Ionic Liquid
IFT	Interfacial Tension (N/m)
IOR	Improved Oil Recovery
ISC	In Situ Combustion
LA	Levulinic Acid
LLE	Liquid-Liquid Extraction
MA	Malonic Acid
MCM	Multiple Contact Miscible
MEA	Monoethanol Amine
MEOR	Microbial Enhanced Oil Recovery
OOIP	Oil Originally In Place
PV	Pore Volume
RF	Recovery Factor
SP	Surfactant-Polymer
SAGD	Steam Assisted Gravity Drainage
SAGP	Steam and Gas Push
TBPB	Tetrabutylphosphonium bromide
VAPEX	Vapor Extraction
WAG	Water Alternating Gas

NOMENCLATURE

N_c	Capillary Number
C	Concentration (ppm or g/m^3)
θ	Contact Angle (degree)
v	Darcy Velocity (m/s)
ρ	Density (kg/m^3)
σ	Interfacial Tension (N/m)
M	Mobility Ratio
λ	Mobility ($\text{m}^3 \cdot \text{s}/\text{kg}$)
S_o	Oil Saturation
k	Permeability (mD or m^2)
Φ	Porosity
P	Pressure (Pa)
k_{ro}	Relative Permeability to Oil (mD or m^2)
k_{rw}	Relative Permeability to Water (mD or m^2)
T	Temperature (K)
μ	Viscosity (cP or $\text{Pa} \cdot \text{s}$)
S_w	Water Saturation

1 INTRODUCTION

1.1 Problem Statement

Consumption of petroleum and other liquid fuels will increase by 32% more from 2010 to 2040 (Al-Wahaibi et al., 2019). To meet increasing energy demand, EOR is an important technique for the production of more oil, especially from heavy oil reservoirs. EOR helps to recover large amounts of oil remained in the reservoir that is not possible to produce with primary and secondary recovery processes.

Thermal EOR methods are the most commonly used EOR method which around 67% of worldwide EOR production comes from this method (Mokheimer et al., 2019). Among thermal methods, steam injection is the most common one. However, they are not economically feasible for deep and thin reservoirs due to extreme heat losses. Moreover, a large amount of steam is required which consumes high energy and produces CO₂ emissions.

Due to these challenges, extensive researches have been conducted about chemical EOR methods. Many researchers showed chemical EOR, particularly surfactant is the most efficient method in many reservoirs. But most of these projects were not commercially successful in industrial applications due to several encountered problems such as high cost, low thermal stability, side reactions of chemicals with reservoir rock and fluids, chemical adsorption onto reservoir rock, and formation damage.

In recent years, ionic liquids (ILs) gained more attention as an alternative to surfactants due to their unique properties such as high thermal stability. But ILs are expensive to apply in industrial scale and some types of them are toxic and not biodegradable. Deep Eutectic Solvents (DESs) were introduced as cheaper and greener alternatives to ILs. However, there are only limited studies about the use of DESs in the EOR process. Therefore, it is necessary to perform a comprehensive study to analyze their performance.

1.2 Objectives

The objectives of this project are:

- i. To evaluate the effectiveness of DESs as a novel EOR method.
- ii. To analyze the performances of DESs considering different EOR processes such as stable emulsion formation, IFT change between oil/brine, wettability alteration, oil recovery improvement, and formation damage
- iii. To compare the performances of DESs in EOR processes.
- iv. To analyze the economic aspect based on chemical EOR methods.

1.3 Thesis Outline

This research consists of six main chapters. Chapter 1 is an introduction that specifies the need for this work and its objectives. Chapter 2 and 3 gives background required about EOR and DESs, respectively. In chapter 2, the types and methods of EOR were reviewed. Chapter 3 gives an overview of the synthesis, types, properties of DESs, and their applications in the oil and gas industry. Chapter 4 introduces all tested DESs in EOR processes. In chapter 5, performances of DESs in EOR processes were evaluated, analyzed, and compared to each other. The report is concluded in chapter 6 and recommendations for future works are given as well.

2 OVERVIEW TO ENHANCED OIL RECOVERY

2.1 Improved Oil Recovery vs. Enhanced Oil Recovery

There is a lot of confusion between the terms Improved Oil Recovery (IOR) and Enhanced Oil Recovery (EOR). Sometimes they are used interchangeably. IOR is defined as any recovery method used to improve oil recoveries by any means, such as horizontal wells and infill drilling, to improve areal and vertical sweep efficiency. EOR can be considered as a subset of IOR. It is a more specific term which implies a reduction in oil saturation below the residual oil saturation (Thomas, 2008). This is important to recover oils retained due to capillary forces after water flooding (in light oil reservoirs) and to produce immobile or nearly immobile oils due to high viscosity (heavy oil reservoirs). In these conditions, recovery can be achieved by lowering the oil saturation below residual oil saturation (Latif et al., 2018).

Thomas (2008) stated the target of EOR varies considerably for the different types of hydrocarbons. Figure 2.1 shows the EOR target for typical light and heavy oil reservoirs and tar sands. For light oil reservoirs, after primary and secondary recovery, most of the oil is not recovered. EOR processes can be used to recover those additional unrecovered amounts of oil. For this type of reservoir, EOR target is around 45% OOIP. For heavy oils and tar sands, only a small amount of oil is recovered from primary and secondary recovery methods and a large amount of production comes from EOR methods.

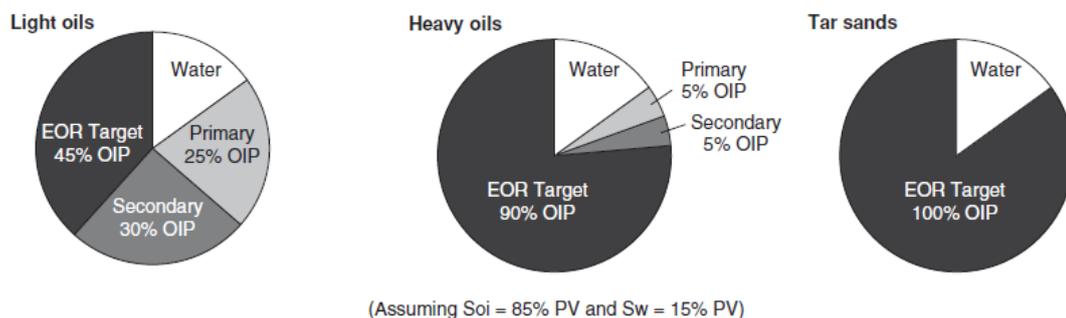


Fig. 2. 1: EOR target for different hydrocarbons
(Source: Thomas, 2008)

From figure 2.1 we can see EOR has an important task for oil recovery enhancement, especially for heavy oil reservoirs. The volume of heavy crude oil in place is around 500 billion barrels that are more than twice of light crude oils (Al-Rujaibi et al., 2016).

According to Zhou et al. (2017), heavy oil production will be increased in the future to meet a continuous increase in energy consumption.

2.2 Recovery of Residual Oil

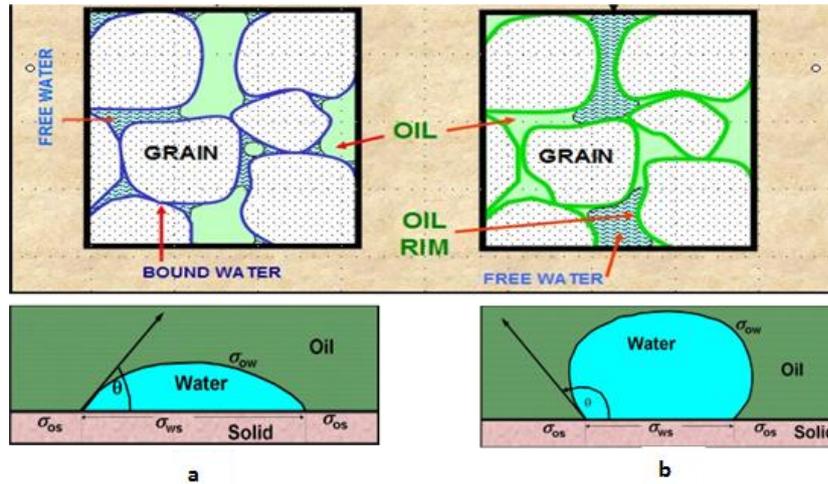
Emulsification

Mandal et al. (2010) defined emulsions as “*Emulsions are suspensions of droplets, greater than 0.1 μm , consisting of two completely immiscible liquids, one of which is dispersed throughout the other*”. The formation and stability of the emulsion are determined by the chemical composition of fluids. Chemicals used in EOR processes promote the emulsification. Moreover, water droplets in oil are promoted if there are surface-active agents in oil such as asphaltene, bases, resins, organic acids which results in the reduction of interfacial tension (Kokal, 2002). In emulsification and entrainment, residual oil saturation is decreased due to the production of oil in water. In emulsification and entrapment, droplets coalesce and block the paths, leads to better sweep efficiency and an increase in oil recovery (Bryan et al., 2008).

Some chemical agents such as surfactants and alkalis can play a role as emulsifying agents with crude oil. This reduces IFT between oil/brine which leads to an increase in oil recovery. This is an advantage in terms of EOR. On the other hand, it has a disadvantage in terms of the separation process. Recovering and recycling the solvents will be difficult due to the formation of stable emulsion (Shuwa et al., 2014).

Wettability

Wettability is defined as “*the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids*” (Anderson, 1986). Reservoir rock can be water-wet, oil-wet, or neutral depending on the preferential wetting phase. Wettability plays an important role in enhanced oil recovery. Oil recovery can be increased by wettability alteration. There are different methods for measurement of wettability such as contact angle measurement and amott tests.



**Fig. 2. 2: (a) Water Wet and (b) Oil Wet Reservoirs
(Source: Crain, 2019)**

According to Anderson (1986), reservoir rock is considered water-wet if the contact angle (θ) is between 0° - 75° , neutral if $75^\circ < \theta < 105^\circ$ and oil-wet if $105^\circ < \theta < 180^\circ$. In rock-liquid-air systems, the system is said liquid wet if the contact angle is between 0° - 75° , neutral if $75^\circ < \theta < 105^\circ$ and air wet if $105^\circ < \theta < 180^\circ$ (Al-Sulaimani et al., 2001).

Interfacial Tension

IFT is force per unit length. The reduction of IFT is an important phenomenon for the enhancement of oil recovery. Chemical agents used in EOR such as surfactants can reduce IFT between the oil/aqueous phase. These results decrease in capillary forces and capillary number increases. After water flooding, large volumes of oil are being trapped due to capillary forces (Zang et al., 2010). An increase in capillary number means an increase in oil recovery. This will be explained in more detail in the following part.

Capillary Number and Mobility Ratio

Capillary number and Mobility Ratio are two main factors that affect the displacement of residual oil. Capillary number is the ratio of viscous forces to capillary forces and is defined by the formula below (Thomas, 2008).

$$Nc = \frac{v * \mu}{\sigma} \quad (2.1)$$

Where:

N_c = Capillary number

v = Darcy velocity (m/s)

μ = Viscosity of displacing fluid (Pa.s)

σ = Interfacial tension (N/m)

Capillary number increases as capillary forces decrease or as viscous forces increase. A practical and most effective way is by reducing interfacial tension. This can be done by applying heat or using suitable chemicals such as surfactants.

Mobility ratio is the ratio of displacing fluid mobility (e.g. water) to the displaced fluid (oil) mobility and defined as below (Thomas, 2008).

$$M = \frac{\lambda (\text{displacing fluid})}{\lambda (\text{displaced fluid})} \quad (2.2)$$

$$\lambda = \frac{k}{\mu} \quad (2.3)$$

Where:

M = Mobility ratio

λ = Mobility of considered fluid

k = Effective permeability (m²)

μ = Viscosity of considered fluid (Pa.s)

Macroscopic (areal and vertical) and microscopic (pore level) displacement efficiencies are affected by mobility ratio. If $M < 1$, the displacement is stable, a piston-like front separates the displaced fluid and displacing fluid phases. If $M > 1$, the displacement is considered unstable (Thomas, 2008). In this case, some of the residual oil is bypassed due to the more easily movement of displacing fluid compared to the displaced fluid. As a result, more displacing fluid is required to obtain the desired residual oil saturation.

2.3 Conventional EOR Methods

When conditions are unfavorable such as heavy oil reservoirs, high IFT, oil-wet conditions, and low permeability reservoirs, additional support is required to enhance oil recovery (Babadagli, 2003). In these cases, enhanced oil recovery processes are required. In light oil reservoirs, oils are trapped due to capillary forces. In heavy oil reservoirs, formation oils are not mobile due to high viscosity. EOR methods help to lower capillary pressure and viscosity. So oil saturation is reduced below residual oil saturation and this leads to the recovery enhancement of crude oils (Thomas, 2008). EOR processes are divided into thermal and non-thermal methods. Reservoir and fluid characteristics play a key role in the suitability of these methods. Normally thermal methods are mostly used for heavy oils and bitumen and non-thermal methods for light oils.

2.3.1 Thermal EOR Methods

Thermal methods increase reservoir temperature and as a result oil viscosity decreases. Oil becomes more mobile and mobility ratio decreases. Besides, some oil vaporizes, and also interfacial tension decreases (Mokheimer et al., 2019). Thermal methods are one of the most advanced EOR methods. Mokheimer et al (2019) reported that around 67% of EOR production comes from thermal methods. Figure 2.3 shows the ratio of different EOR projects in the world.

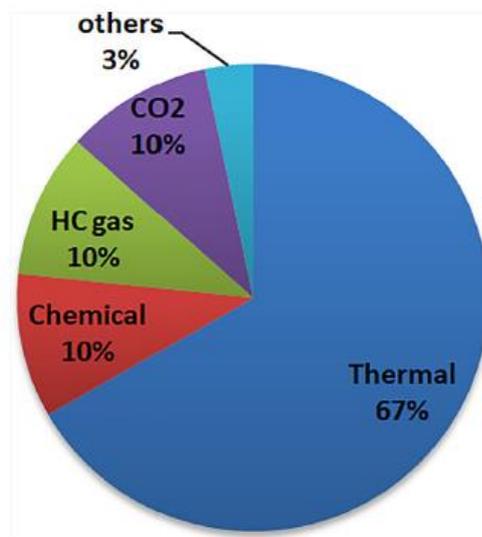


Fig. 2. 3: Ratio of Different EOR Methods used in the World
(Source: Mokheimer et al, 2019)

Thermal methods are best suited for heavy and ultra-heavy oils with API gravities less than 20° (Thomas, 2008, Mokheimer et al., 2019). The main thermal EOR methods are hot water flooding, steam-based injection, in situ combustion, and electrical heating. Figure 2.4 shows the classification of thermal EOR.

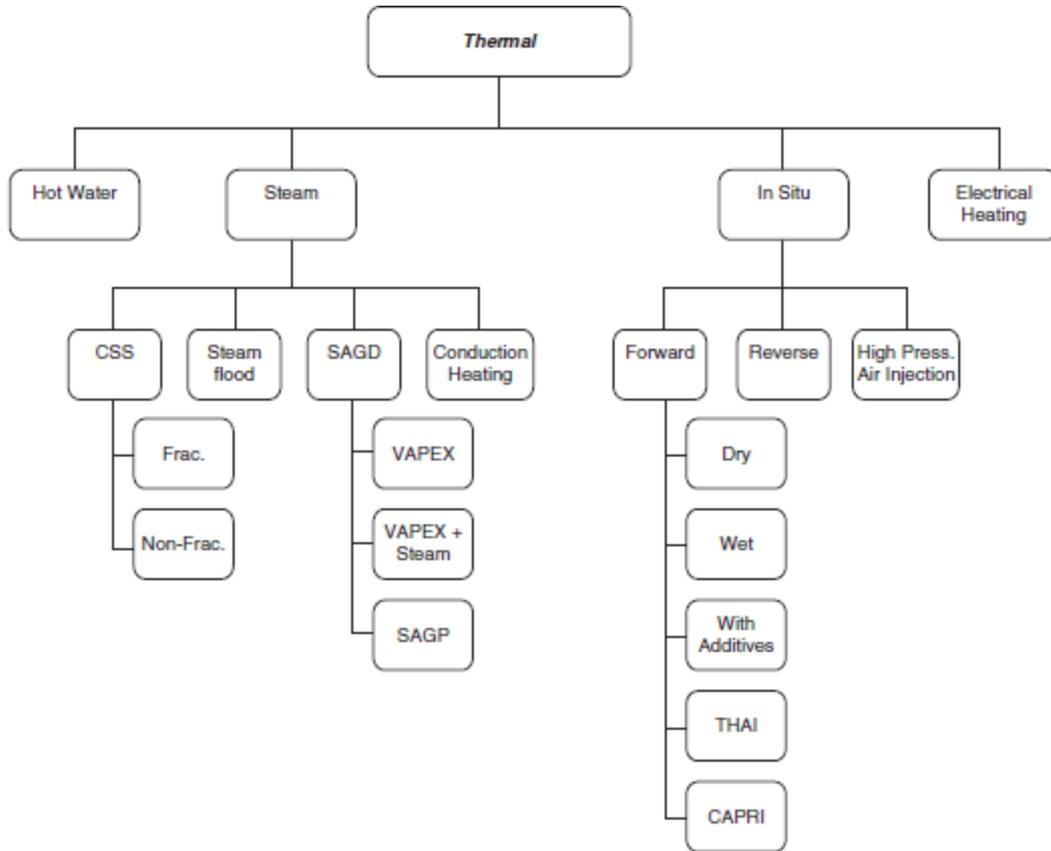


Fig. 2. 4: Classification of Thermal EOR
(Source: Thomas, 2008)

Steam-based methods are most common among thermal EOR methods due to the fact that it has been more commercially successful compared to the others. Below are subdivisions of main steam-based methods.

Cyclic Steam Stimulation (CSS)

In the cyclic steam stimulation process single well is used for the injection of steam and production of oil. CSS divided into three steps as shown in figure 2.5.

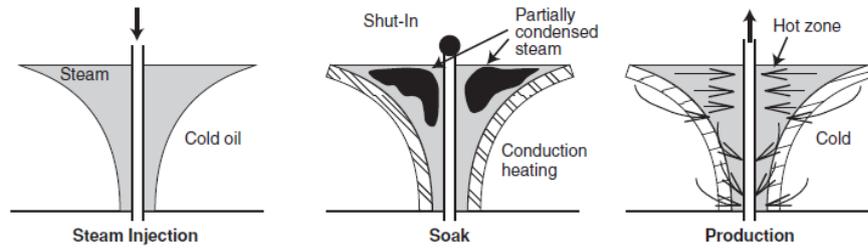


Fig. 2. 5: Cyclic Steam Stimulation Stages
(Source: Thomas, 2008)

Initially, steam is injected for a certain period of time (usually a month). This results in the heating of oil around well and reduction of viscosity. After that, the distribution of heat within the reservoir is achieved by shutting in the well for a few days. This stage is called soak. Then the well opened for production. The oil rate is high at the beginning but after a few months declines due to a decrease in temperature that results in an increase of oil viscosity again. In order to raise reservoir temperature, another cycle can be started and repeated several times. Mokheimer et al (2019) presented the main advantage of this method is rapid pay-out during early production. On the other hand, the main limitation of this method is oil recovery is low ranging from 10-20% OOIP (Mokheimer et al., 2019).

Steam flooding

The difference between steam flooding from cyclic steam stimulation is in this method more than one well used. Steam is injected from the injection well. This moves slowly and heats the formation, decreases the viscosity of the oil, and displaces oil towards the production well. Schematic is shown in figure 2.6.

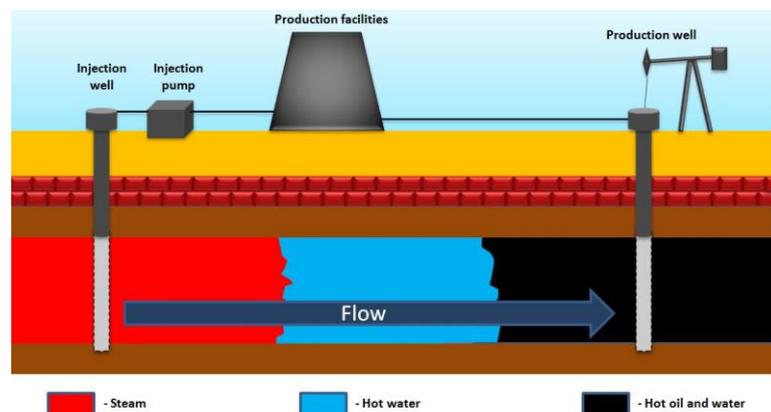


Fig. 2. 6: Schematic of Steamflooding Process
(Source: Zerkalov, 2015)

Compared to cyclic steam stimulation, steam flooding process is more costly because a larger amount of steam is required. Nevertheless, with this process oil recovery is higher which is around 50-60% OOIP (Zerkalov, 2015).

Steam Assisted Gravity Drainage (SAGD)

This method involves using two horizontal wells that are drilled parallel to each other. The distance between the two wells is around 5 m. Top well is intended for steam injection and bottom well for production. Figure 2.7 shows schematic representation.

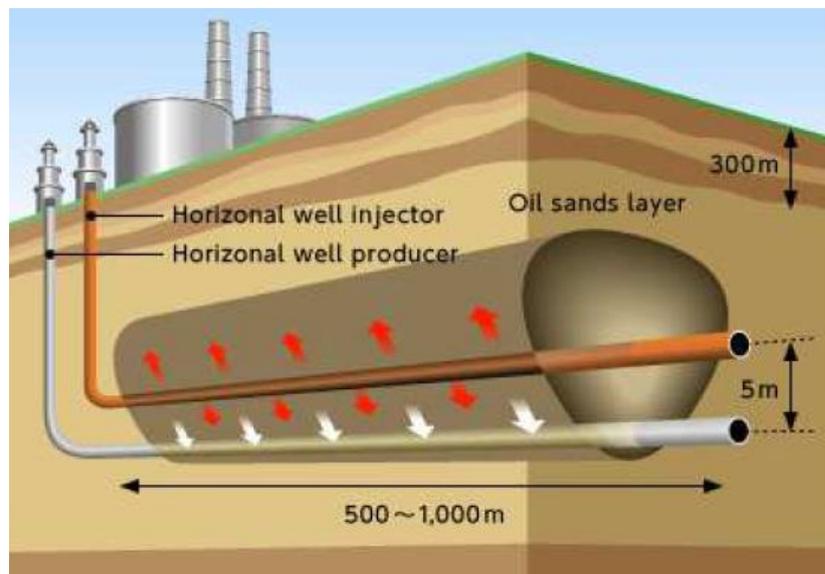


Fig. 2. 7: Schematic of Steam Assisted Gravity Drainage (SAGD)
(Source: Ahmedzhanov, 2013)

Steam is continuously injected that forms a steam chamber due to the rise of steam to the top of the formation. This heats the formation and heavy oil becomes mobile and falls down due to gravity. This is recovered from the production well. Vertical permeability of the formation is important for the success of this method. The limitation of this method is its cost and environmental issues. Large amounts of water are required for the generation of steam and also a quite high amount of natural gas necessary (Thomas, 2008).

There are different variations of SAGD such as Vapor Extraction (VAPEX), Expanding Solvent SAGD (ES-SAGD), and Steam and Gas Push (SAGP) in which solvents, gasses, and vapors are used. Manrique et al (2010) stated these methods are not commercially proven yet.

In Situ Combustion (ISC)

This method is also called fire flooding. In this method oxidizer, fuel and igniter are used. Compressed air or oxygen is injected into a reservoir that burns some portion of oil. Oil viscosity decreases dramatically due to a very high temperature. Schematic is shown in figure 2.8.

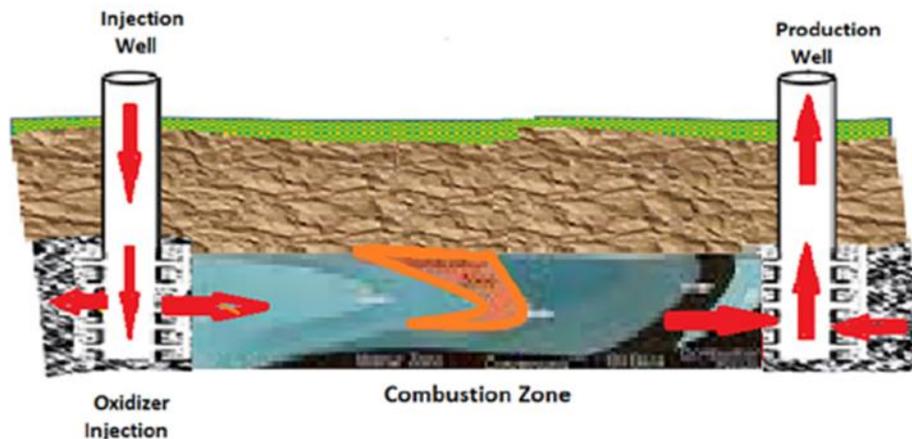


Fig. 2. 8: Schematic illustration of In Situ Combustion Process
(Source: Mokheimer et al, 2019)

The main advantages of the ISC than steam injection are less energy consumption, no need for water recycling, more environmentally friendly, and improved heat transfer efficiency (Alade et al., 2020). In situ combustion has been tested in many places, however, very few projects have been economical and none has advanced to commercial scale (Thomas, 2008). There are two main types of ISC. Forward and reverse combustion depending on a combustion front. In forward type, near the injection well ignition happens, combustion front and airflow move in the same direction towards the production well. Whereas in reverse type, ignition happens near the production well, combustion front and airflow move in the opposite direction (Thomas, 2008).

2.3.2 Non-Thermal EOR Methods

Non-thermal methods can be divided into four main groups as shown in figure 2.9. Miscible gas, chemical, immiscible gas injection processes, and others. The more notable among other methods are Microbial EOR (MEOR) and Foam flooding.

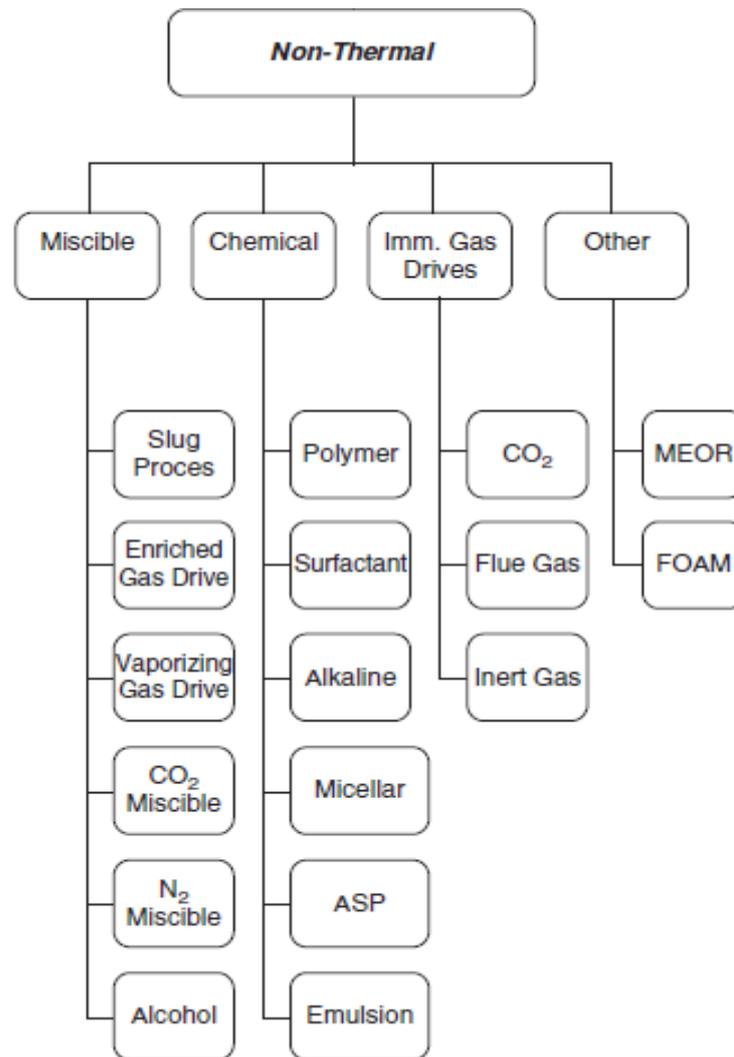


Fig. 2. 9: Non-Thermal EOR Methods
(Source: Thomas, 2008)

Miscible Flooding

In this method injected displacing fluid is miscible with displaced fluid (oil). Interfacial tension is eliminated in the miscible process, thus capillary forces are zero. Residual oil and displacing fluid mixes and forms one phase. Since interfacial tension is zero, capillary number becomes infinite, and residual oil saturation can be reduced down to zero. As a result oil recovery increases. Miscibility can occur at first contact (FCM) or after multiple contacts (MCM). There are different miscible recovery methods such as miscible slug process, enriched gas drive, vaporizing gas drive, CO₂, and N₂. Figure 2.10 shows a schematic of the process.

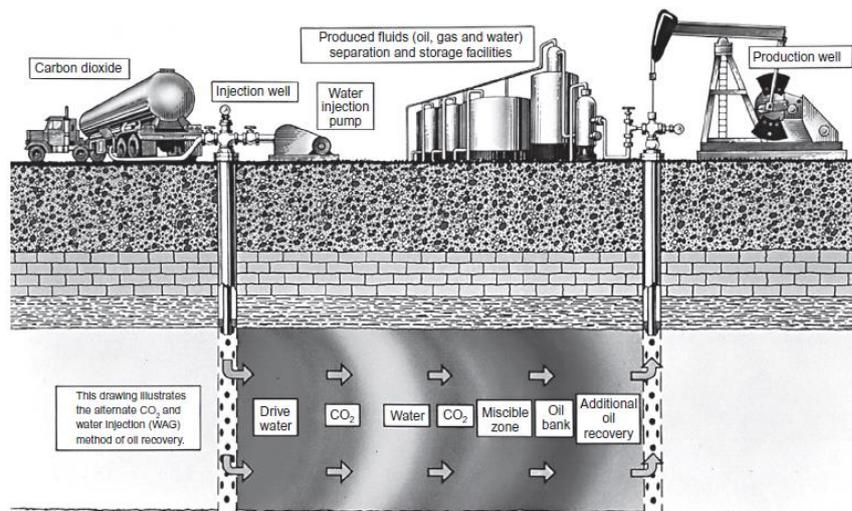


Fig. 2. 10: Schematic Illustration of Miscible Flooding
(Source: Speight, 2016)

Chemical EOR

Chemical EOR or chemical flooding uses chemicals such as polymer, surfactant, alkali to recover more oil. Water-soluble polymers reduce the mobility of injected water by increasing its viscosity that improves sweep efficiency. Surfactants decrease interfacial tension which results a decrease in capillary forces and more oil becomes mobile. Alkali reduces interfacial tension by reacting with organic acids in the oil and generates in-situ surfactants. Surfactants are considered more efficient compared to polymer or alkali, but the best performances were obtained when three of them used together (alkali/surfactants/polymer flooding) (Thomas and Faruq Ali, 2001).

Surfactants decrease interfacial tension between oil and water and also alter wettability. These results decrease in capillary forces and more oil becomes mobile. Oil recovery improves up to 60–70% OOIP (Bera and Belhaj, 2006). This increased attention of researchers about surfactant flooding.

Several projects were done all around the world about chemical EOR but most of them were economically unsuccessful. Another challenge was the lack of availability of compatible chemicals to high pressure and a high saline environment. China is the only place where successful results of chemical EOR, especially polymer has been obtained (Kokal and Al-Kaabi, 2010).

Water Alternating Gas (WAG)

This process consists of a gas injection followed by water injection to increase oil recovery. Gas and water injections are performed from the same injection well and injected gas can be miscible or immiscible. Figure 2.11 shows schematic representation.

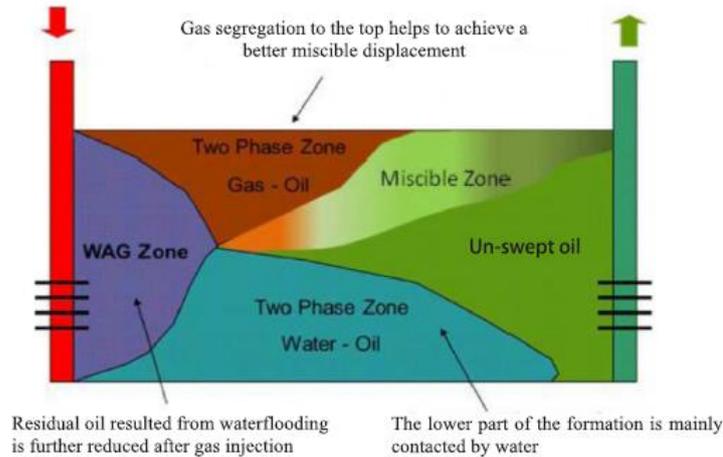


Fig. 2. 11: Schematic Representation of WAG Injection
(Source: Afzali, 2018)

When displacing fluid is gas, the mobility ratio is very high because of the high mobility of gas. The presence of the water phase reduces effective permeability to the injected gas and the mobility ratio of displacement is improved. First slug of gas is injected to reduce residual oil saturation. After that, a slug of water is injected. This process repeated every certain period of time (usually three or six months). Displacement efficiency increases due to gas injection and sweep efficiency increases due to water injection.

2.4 Ionic Liquids as an Alternative to Surfactants in Chemical EOR

Even though some chemicals improve oil recovery, there are several problems encountered. Major problems are formation damage, side reactions of chemicals with reservoir rock and fluids, chemicals adsorption onto reservoir rock (usually for surfactants), high injectivity (for polymers) and high cost (Thomas, 2008, Mohsenzadeh et al., 2015b, Al-Wahaibi et al., 2019). Considering these challenges, extensive studies have been conducted to find alternatives. In the latest years, ionic liquids gained more attention as an alternative to surfactants due to their unique properties such as high thermal stability. Abbott et al. (2008) defined ionic liquids as “*Ionic liquids are salts*

with anionic and cationic components that have a very low melting temperature, thus, treats as liquids at ambient temperature". Due to their aromaticity and ionic nature, they proved to enhance oil recovery significantly (Pereira et al., 2014). Figure 2.12 shows the number of publications on the application of ionic liquids in the upstream oil industry from January 2009 to September 2019. From the figure, we can see publications are increasing in recent years for EOR.

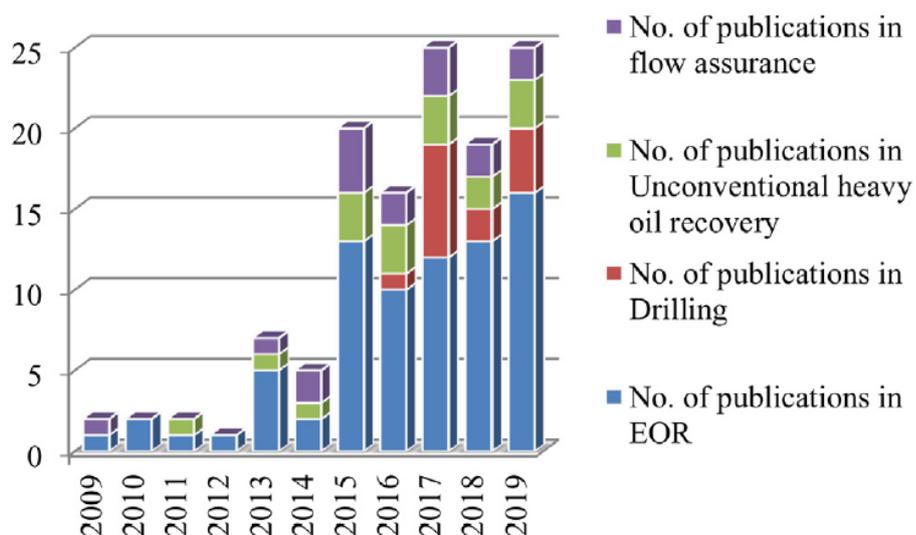


Fig. 2. 12: Publication Record on Application of ILs in Upstream Oil Industry
(Source: Bera et al., 2020)

Ionic liquids are organic salts having a melting point below 100 °C and they are often found as a liquid up to a moderate temperature (Pillai et al., 2018). Johnson (2007) defined the modern ionic liquids as the “*volatile organic solvents with low vapor pressure and moderate specific conductivity*” and documented their properties as in table 2.1.

Tab. 2. 1: Properties of Modern Ionic Liquids
(Source: Johnson, 2007)

A salt	Cation and or anion quite large
Freezing point	Preferably below 100 °C
Liquidus range	Often >200 °C
Thermal stability	Usually high
Viscosity	Normally <100 cP, workable
Dielectric constant	Implied <30
Polarity	Moderate
Specific conductivity	Usually < 10 mScm ⁻¹ , “Good”

Molar conductivity	<10 Scm ² mol ⁻¹
Electrochemical window	>2 V, even 4.5 V, except for Brønsted acidic systems
Solvent and/or catalyst	Excellent for many organic reactions
Vapor pressure	Usually negligible

Reduction of interfacial tension and alteration of wettability are mechanisms of surfactant flooding due to their surface-active properties. ILs also have an ability to reduce IFT and form micelle which makes them alternative surfactants for EOR (Bera and Belhaj, 2016). Table 2.2 shows the comparison between ionic liquids and surfactants for EOR purposes.

**Tab. 2. 2: Comparison of ILs and Surfactants for EOR Purpose
(Source: Bera and Belhaj, 2016)**

Properties	Ionic liquids	Surfactants
IFT	Some surface active ionic liquids can reduce IFT up to 10 ⁻² mN/m. it is necessary to enhance the surface activity of ionic liquids for application in EOR.	They can reduce IFT up to 10 ⁻⁴ -10 ⁻³ mN/m to show their effectiveness in EOR applications.
Viscosity	The viscosity of some ionic liquids can be manipulated by variations in branching and higher viscosity can be expected.	In aqueous solution, they cannot produce higher viscosity.
Stability	Some ionic liquids are stable over a long temperature range and can be stored without decomposition for a long time.	Stability of surfactants at high temperature is always questionable.
Dissolution Power	Ionic liquids can dissolve even gases like H ₂ , CO, and CO ₂ . They can be used even under supercritical CO ₂ . So they may be considered in water alternating gas flooding replacing water.	Surfactants cannot dissolve these gases.

3 OVERVIEW TO DEEP EUTECTIC SOLVENTS

Search for green chemical solvents are always in progress. Abbot et al. (2003) introduced the deep eutectic solvents (DESs) and defined it as a new generation sustainable solvents and a potential alternative to ionic liquids and conventional organic solvents. Fundamental properties of DESs are similar to ILs such as density, viscosity, conductivity, surface tension, high thermal stability, and negligible volatility (Abbot et al., 2003, Hayyan et al., 2013, Mohsenzadeh et al. 2014). DESs are cheaper, easy to prepare, and more environmentally friendly compared to ILs (Zhang et al., 2012). They are recyclable, biodegradable, non-corrosive, and non-flammable (Al-Rujaibi et al., 2016).

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*” (Atkins and De Paula, 2006). Eutectic point is the intersection of eutectic composition and eutectic temperature as shown in figure 3.1.

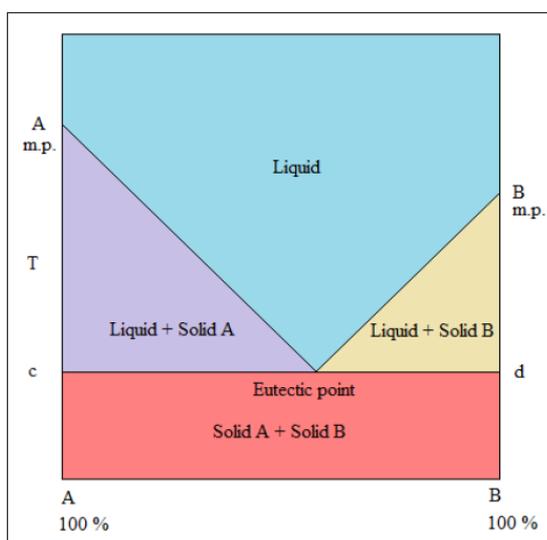


Fig. 3. 1: Schematic of a Eutectic Point on a Two-Component Phase Diagram (Source: Atkins and De Paula, 2016)

DES is composed of at least two cheap and safe components that are able to form a eutectic mixture in which the melting point is lower than its individual components (Abbot et al., 2003).

3.1 Synthesis of DES

DESs are obtained by mixing HBA and a HBD at a proper molar ratio (El Achkar et al., 2019). The mechanism by which a DES is formed is not complicated. The HBD interacts with the anion of the HBA (salt) and increases its effective size, which in turn reduces the anion interaction with the cation. Thus, the melting point of the mixture is decreased (Zhang et al., 2012, Carriazo et al., 2012). “Generally, DESs are characterized by a large depression of freezing point and by being liquids at temperatures lower than 150°C” (Carriazo et al., 2012). However, at the temperature between 22°C and 70°C, most of them are in liquid form (Zhang et al., 2012, Carriazo et al., 2012). Figure 3.2 shows the most common salts and HBDs used for DES synthesis.

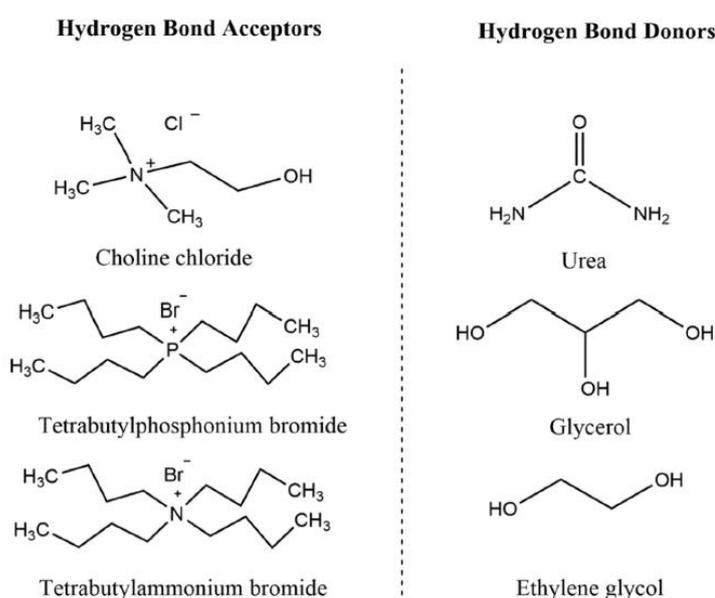


Fig. 3. 2: Most Common Salts and Hydrogen Bond Donors used for DES Synthesis (Source: El Achkar et al., 2019)

The most studied DES constituents are choline chloride and urea which was first introduced by Abbott and co-workers in 2003. The melting points of choline chloride is 302°C and urea is 133°C. When mixed at a 1:2 molar ratio of choline chloride:urea, a liquid eutectic mixture was formed as shown in figure 3.3 and that has a melting temperature of 12 °C that is considerably lower than that of either of the constituents as shown in figure 3.4 (Abbot et al., 2003).

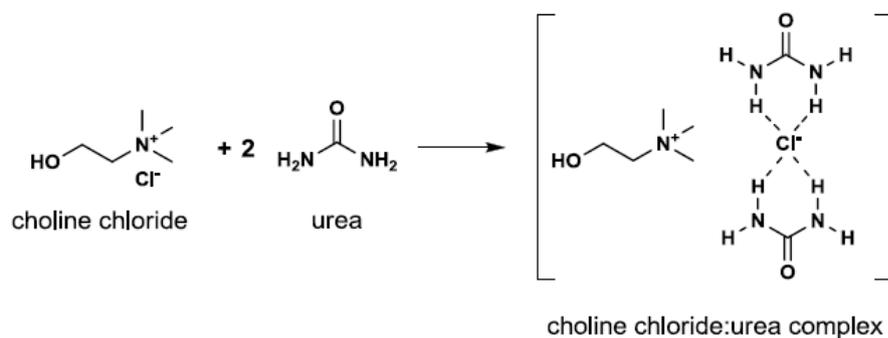


Fig. 3. 3: Formation of Deep Eutectic Solvent
(Source: Abbot et al., 2003)

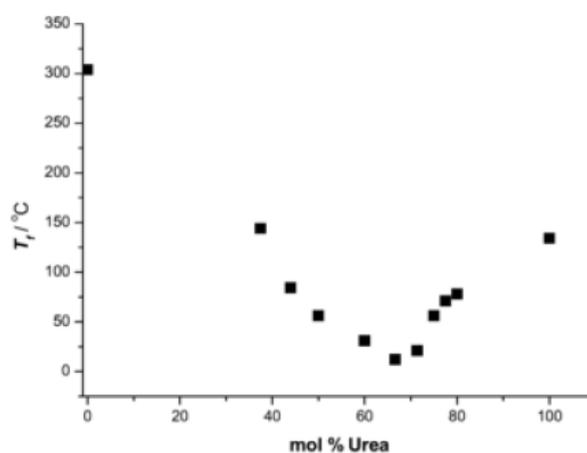


Fig. 3. 4: Melting Point of ChCl:Urea Mixtures as a Function of Composition
(Source: Abbot et al., 2003)

Choline chloride is considered green and it doesn't have any harmful effects (Aquilina et al., 2011). It is mostly used as a vitamin for animals. Urea (carbamide) is a well-known fertilizer which is used in agriculture. Since both constituents are harmless and green when mixed resulting DES is also totally green (Mavrovic et al., 2010).

Heating and grinding methods are two main types of methods that are used for the preparation of DES (Florindo et al., 2014). The heating method is the most common one in which compounds are mixed and heated at 100 °C with constant stirring until clear liquid is achieved. In grinding method compounds are mixed at room temperature and grinded with a pestle in a mortar until a homogeneous liquid is formed.

DESs are produced without chemical reactions and without the need for catalysts. While, the production of ILs involves chemical reactions of the raw materials and side

products will form impurities to the IL and require additional purification (Keskin et al., 2007). Unlike traditional ILs, preparation of DESs are simple just by mixing and heating the compounds under stirring without the need for a catalyst. Moreover, total mass efficiency and zero-emission in the synthesis are achieved. This means that all the masses of the salt and HBD involved are converted to DES, which is environmentally friendly as there are no side products, especially in the form of vapors (Kareem et al., 2010, Hayyan et al., 2012, Zhao and Baker, 2013).

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 vapor pressures and most of their components are non-toxic and biodegradable (Weaver et al., 2010, Hayyan et al., 2013). All these advantages increased interest in deep eutectic solvents as greener alternatives for ionic liquids. Gurkan et al. (2019) reported the number of publications and citations for DES by June 24, 2019, as shown in figure 3.5. We can see that researches in this area increase significantly during recent years.

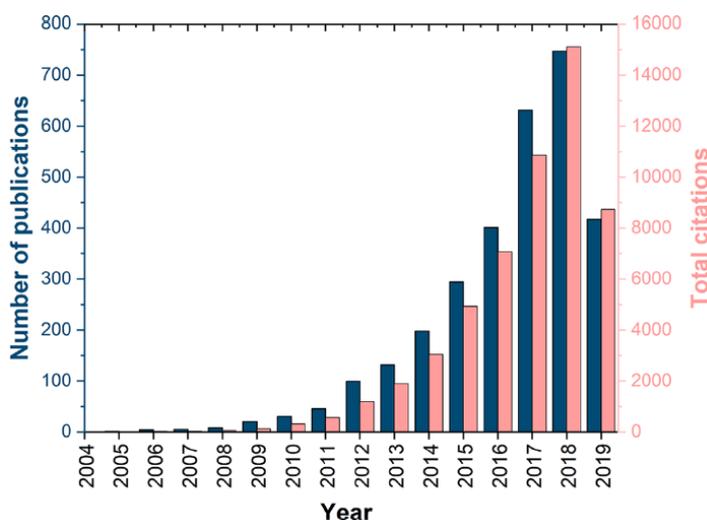


Fig. 3. 5: Total Publications and Citations for DES by June 24, 2019
(Source: Gurkan et al., 2019)

3.2 Types of DES

DESs are classified into four main types. Smith et al. (2014) showed the classification of DESs using the general formula Cat^+X^-zY , where Cat^+ is a cation, X^- is an anion, and Lewis or Brønsted acid Y (z refers to the number of Y molecules that

interact with the anion). Table 3.1 shows DESs formed from MCl_x and quaternary ammonium salts (Smith et al., 2014).

**Tab. 3. 1: Types of Deep Eutectic Solvents
(Source: Smith et al., 2014)**

Types	General formula	Terms	Example
Type I	$Cat^+X^- + zMCl_x$	$M = Zn, In, Sn, Al, Fe$	$ChCl + ZnCl_2$
Type II	$Cat^+X^- + zMCl_x \cdot yH_2O$	$M = Cr, Ni, Cu, Fe, Co$	$ChCl + CoCl_2 \cdot 6H_2O$
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.

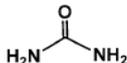
Type IV: Composed of metal salts and HBD.

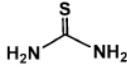
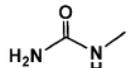
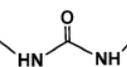
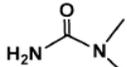
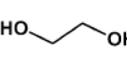
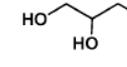
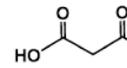
3.3 Properties of DESs

3.3.1 Freezing Point

The low freezing point of DESs is one of their important property which makes them unique. As mentioned earlier Abbot et al. (2003) showed the formation of a unique solvent with freezing point $12\text{ }^\circ\text{C}$ that is considerably lower than its components when mixed at a 1:2 molar ratio of choline chloride:urea. Moreover, Kareem et al. (2010) presented a solvent formation with a melting point of $-66\text{ }^\circ\text{C}$ from 1:2 molar ratio of choline chloride:ethylene glycol. Table 3.2 shows the list of freezing points (T_f) for common $ChCl$ -based DESs. (T_m^* : melting point of pure HBD).

**Tab. 3. 2: Freezing Point (T_f) of Common $ChCl$ -based DESs.
(Source: Zhang et al., 2012)**

Hydrogen bond donor (HBD)	$ChCl$: HBD (molar ratio)	$T_m^*/^\circ\text{C}$	$T_f/^\circ\text{C}$
 Urea	1 : 2	134	12

	Thiourea	1 : 2	175	69
	1-Methyl urea	1 : 2	93	29
	1,3-Dimethyl urea	1 : 2	102	70
	1,1-Dimethyl urea	1 : 2	180	149
	Ethylene glycol	1 : 2	-12.9	-66
	Glycerol	1 : 2	17.8	-40
	Malonic acid	1 : 1	135	10

El Achkar (2019) pointed out that selection HBA, HBD, and their molar ratios are the main parameters that affect the freezing point of DESs.

3.3.2 Viscosity

DESs have high viscosity due to the hydrogen bonding between components which reduces the mobility of compounds (Zhang et al., 2012). Van der Waals or electrostatic forces might cause high viscosity as well. Table 3.3 shows the viscosities of common DESs at different temperatures.

Tab. 3. 3: Viscosities of Common DESs at different Temperatures
(Source: Zhang et al., 2012)

Organic Salts	HBD	Salt : HBD molar ratio	Viscosities (cP)
ChCl	Urea	1 : 2	750 (25 °C)
ChCl	EG	1 : 2	37 (25 °C)
ChCl	Glycerol	1 : 2	259 (25 °C)
ChCl	Malonic acid	1 : 2	1124 (25 °C)
ZnCl ₂	Urea	1 : 3.5	11 340 (25 °C)

The viscosity of a eutectic mixture is mainly affected by the nature of its components such as the salt/HBD molar ratio, the temperature, and the water content (El Achkar et

al., 2019). Florindo et al. (2014) showed that by adding water to the system, the viscosity decreases drastically around 10-30 times. At 25 °C, by hydrating ChCl:urea with 6 wt% water, viscosity reduced 13 times compared to the viscosity of dry ChCl:urea (Du et al., 2016).

Du et al. (2016) studied the effect of water (2.5–20 wt%) on three ChCl-based DESs, namely (1) Reline (ChCl:urea), (2) Ethaline (ChCl:ethylene glycol) and (3) Glyceline (ChCl:glycerol) as shown in figure 3.6.

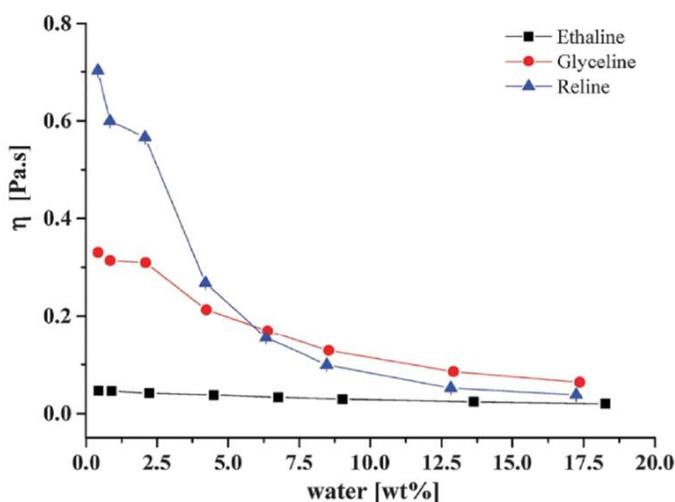


Fig. 3. 6: Effect of Water Content on Viscosity for ChCl-based DESs at 20 °C (Source: Du et al., 2016)

It was observed that with increasing water content viscosity decreased in all liquids. However, the decrease is not steady. The effect of water on the viscosity of Reline is greater than the other two liquids. Whereas, there is a small effect for Ethaline (Du et al., 2016).

Abbott et al. (2011) showed the effect of ChCl concentration and temperature on viscosity of ChCl:glycerol mixture as shown in figure 3.7. The viscosity of pure glycerol (without ChCl) is around 1200 cP. It can be observed from figure viscosity decreases by increasing temperature and ChCl concentration. A significant decrease of glycerol viscosity by the addition of ChCl was explained as due to the partial break of a strong hydrogen bond network of glycerol.

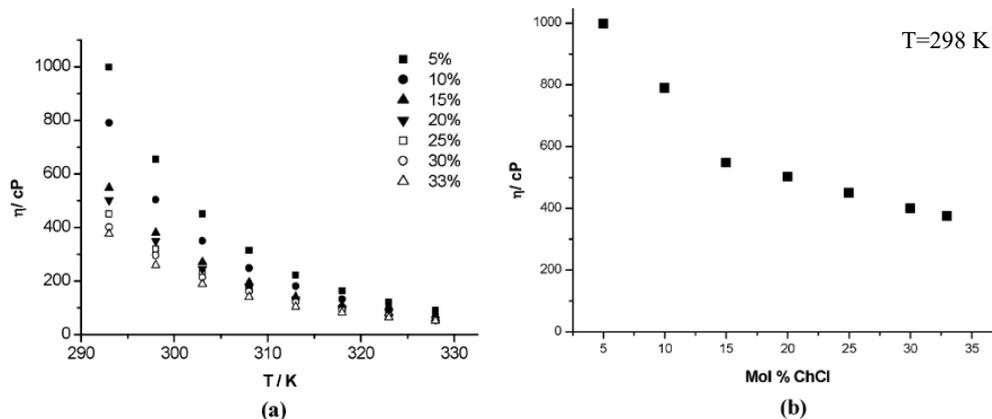


Fig. 3. 7: Effect of Temperature (a) and ChCl concentration (a and b) on Viscosity (Source: Abbott et al., 2011)

3.3.3 Density

Several studies were performed for the measurement of densities of DESs as a function of temperature (Abbott et al., 2011, Shahbaz et al., 2012, Hayyan et al., 2013, Florindo et al., 2014). Results showed that density decreases with increasing temperature which is the same behavior as most of the liquid phase materials. The range of density of common DESs varies between 1.04-1.63 g/cm³ at 25 °C and the salt/HBD molar ratio has a significant effect (El Achkar et al., 2019). Table 3.4 shows density values for common DESs at 25 °C.

Tab. 3. 4: Densities of Common DESs at 25 °C (Source: Zhang et al., 2012)

Salts	HBD	Salt : HBD (mol : mol)	Density (ρ , g cm ⁻³)
ChCl	Urea	1 : 2	1.25
ZnCl ₂	Urea	1 : 3.5	1.63
ZnCl ₂	EG	1 : 4	1.45
ChCl	Glycerol	1 : 2	1.18
ChCl	EG	1 : 3	1.12
ChCl	Malonic acid	1 : 2	1.25

3.3.4 Conductivity

Most of DESs have low ionic conductivities (lower than 2 mS cm⁻¹ at 20 °C) due to their relatively high viscosity (El Achkar et al., 2019). Table 3.5 shows ionic conductivity values for common DESs at different temperatures.

Tab. 3. 5: Ionic Conductivities of Common DESs
(Source: Zhang et al., 2012)

Salts	HBD	Salt : HBD (mol : mol)	Conductivity (κ , mS cm ⁻¹)
ChCl	Urea	1 : 2	0.199 (40 °C)
ChCl	EG	1 : 2	7.61 (20 °C)
ChCl	Glycerol	1 : 2	1.05 (20 °C)
ZnCl ₂	Urea	1 : 3.5	0.18 (42 °C)

Viscosity of DES decreases with increasing temperature which results in the increase of ionic conductivity. Moreover, the ionic conductivity of DES increases with increasing water content due to the decrease of viscosity.

3.4 Applications of DESs in Oil and Gas Industry

Since the introduction of DES at the beginning of the 21st century, their applications of areas are widening due to their advantages. The main advantages of DESs compared to ionic liquids can be summarized as lower cost, non-toxicity, easy preparation, biodegradability, and elimination of purification step. Ge et al. (2017) presented the distribution of DES research topics in different research fields as shown in figure 3.8.

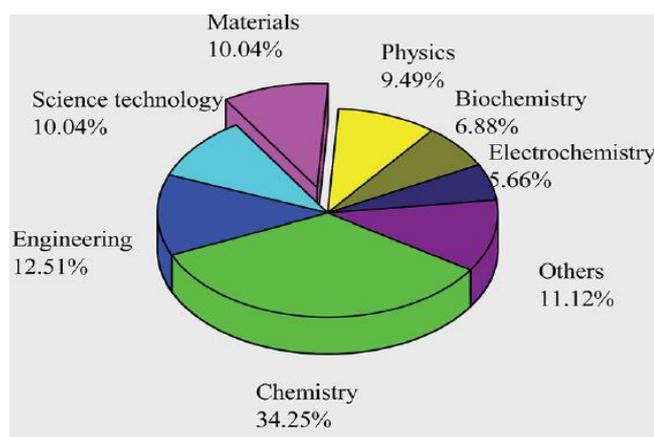


Fig. 3. 8: DES Research Topics in Different Fields
(Source: Ge et al., 2017)

Even though the main research area of DESs is chemistry, interests in other fields are 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 pharmacy (El-hoshoudy et al., 2019, Feng et al., 2019). Important applications of DESs in oil and gas fields can be presented as below.

3.4.1 DESs for Efficient Separation Processes

3.4.1.1 *Dearomatization*

The separation of aromatic from aliphatic compounds is important in order to improve fuel properties and to 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 low cost, simple operation, and low energy consumption. In this method selection of extractant 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 having green and efficient separation (Feng et al., 2019).

Ionic liquids have been studied as an alternative to organic solvents by several researchers (Meindersma et al., 2006, 2010, Arce et al., 2007, Pereiro et al., 2009, 2012, Zheng et al., 2014, Smiglak et al., 2014, Zhang et al., 2016, Addouni et al., 2020). Improved separation performance was achieved with most of ILs compared to organic solvents. But due to 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.

Kareem et al. (2012) studied the toluene and heptane separation using DES composed of tetrabutylphosphonium-bromide and ethylene glycol. Tests were performed at different temperatures and different molar ratios of salt:HBD. 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. (2014) performed the separation of BTEX aromatics from n-octane using tetrabutylammonium bromide/sulfolane DES. From 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. (2015) investigated the separation of toluene from the toluene and n-hexane (or cyclohexane) mixtures using DES consisting of tetrabutylphosphonium bromide (TBPB) and levulinic acid (LA) at different temperatures and molar ratios. Optimal condition was achieved with levulinic acid:TBPB (6:1) and 6.4:1 molar ratio of DES:toluene at room temperature. By distillation at 100 °C recovery of toluene in DES was possible and DES was reused. It was concluded that the separation by DESs showed high selectivity and extraction rate.

Gouveia et al. (2016) evaluated the separation of toluene from n-heptane with liquid-liquid extraction method using DESs. DESs were ammonium salt-based (cholinium chloride, benzylcholinium chloride, and tetrabutylammonium chloride) as HBA and levulinic acid as HBD with the 1:2 mole ratio of HBA:HBD. Improvement of distribution coefficient accomplished by the introduction of more hydrophobic HBA and higher selectivity achieved by playing with the aromaticity of the DES.

Larriba et al. (2017) tested aromatic HCs extraction from reformer using choline chloride-based DES. In this study, six ChCl-based DESs (ethylene glycol, glycerol, levulinic acid, phenylacetic acid, malonic acid, 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. (2019) studied the effective separation of aromatic hydrocarbons by pyridine-based deep eutectic solvents. By liquid-liquid extraction method, ternary systems were studied. N-formyl morpholine DES showed better separation performance compared to levulinic acid. The best separation for both DESs were at low temperatures (20 °C) and low aromatic concentration.

3.4.1.2 *Desulfurization*

Sulfur dioxide (SO₂) is a harmful gas to the human health and ecosystem. It is produced by the combustion of sulfur-containing fuels such as coal, oil, or diesel. Exposure to SO₂ causes several health problems such as asthma, neurological disorders, wheezing, and irritation to the skin are only some of them (Sang et al., 2010, Han et al., 2018). Moreover, SO₂ damages the ecosystem as a result of acid rain. Due to these reasons, numerous regulations have been imposed to reduce SO₂ emissions. Maximum Sulphur content that is allowed in the fuel is one of these regulations. In recent years more strict policies are being taken (Chandran et al., 2019).

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 is the most common method for the removal of sulfur from crude oil but polycyclic organic sulfides can't be removed with this method (Breyssa et al., 2003, Li et al., 2013, Chandran et al., 2019). Due to these reasons and also due to the simplicity of the process, low energy consumption researches on the solvent extraction technique is increasing. In this method, solvents are used to remove Sulphur compounds from the hydrocarbon stream based on 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, recent years DESs gained more attention as an alternative.

Li et al. (2013) reported the first paper on DESs as a solvent for desulfurization. Desulfurization of fuels was carried out with ammonium-based DESs. Successful desulfurization of fuels was achieved from these DESs. Tetrabutyl ammonium chloride: polyethylene glycol showed the optimum condition with an extraction efficiency of 83% for one cycle that is significantly higher than traditional solvents and ILs. Moreover, the amount of Sulphur in fuels decreased below 8.5 ppm.

Using FeCl_3 -based DES, Gano et al. (2015) studied the simulated fuel and commercial diesel desulfurization. As a sulfur compound, dibenzothiophene and thiophene were present in 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 desulfurization of real commercial diesel was performed using the same solvents. 32% of sulfur removed from diesel. Additionally, it was concluded also DESs could be regenerated and used repetitively.

Makos and Boczka (2019) successfully applied DES (ChCl:phenol) for the desulfurization of model liquid fuel which contains thiophene, benzothiophene, and dibenzothiophene. The best conditions were 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%.

3.4.1.3 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 (Warrag et al., 2017). 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 the diesel engine (Smith et al., 2014). Glycerol is highly polar unlikely biodiesel. Liquid-liquid phase decantation is a common method for separation of glycerol but non-negligible amount remains and extra-treatments are required (Zhang et al., 2012).

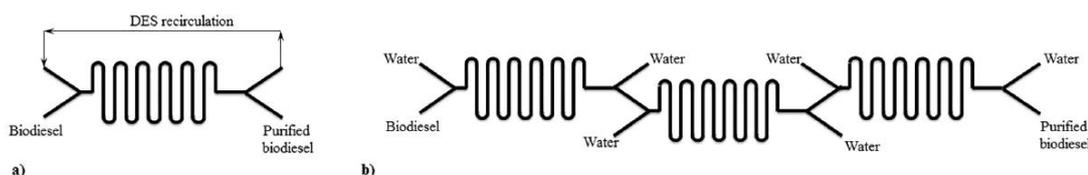
Abbott et al. (2007) studied the removal of glycerol from biodiesel in two ways. Initially, they added pure quaternary ammonium salt to glycerol containing biodiesel to form eutectic mixture with glycerol. This approach was not successful. It was stated this might be due to enthalpy formation. After 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 25% of choline chloride could be recovered.

Shahbaz et al. (2010) used different ChCl-based DESs to separate glycerol from palm oil-based biodiesel. All DESs showed successful results which removed all free glycerol with an efficiency of >99%. Moreover, Shahbaz et al. (2011) reported the removal of residual catalyst (KOH) from palm oil-based biodiesel using DESs in another paper.

Niawanti et al. (2017) performed a purification of biodiesel using ChCl-based DESs. DES was a mixture of 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.

Salic et al. (2020) evaluated the biodiesel purification in micro extractors using water washing method and also using seven different DESs that is based on a ChCl:glycerol and ChCl:ethylene glycol mixtures. Three different sizes of micro extractors were used

for both methods. Results from both processes were compared with each other. DESs showed advantages over water washing methods such as higher efficiency, a lower amount of solvent usage, and less waste treatment. It was possible to separate purified diesel and DES at the end of the micro extractor and recirculate DES. Figure 3.9 shows the graphical illustration of processes.



**Fig. 3. 9: Glycerol Removal Using (a) DES and (b) Water Washing
(Source: Salic et al., 2020)**

3.4.1.4 CO₂ 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 CO₂ gas is one of the major causes of global warming. Several technologies have been studied that are free of CO₂ emission. But most of them are not yet at the stage of large scale implementation. On the other hand, a large number of techniques and researches are being conducted for the CO₂ capture. Fossil fuels are the main cause of CO₂ emissions which is the most important energy source. Hence, reducing CO₂ emissions from industry is essential.

CO₂ capture using aqueous ethanolamine solutions such as monoethanol amine (MEA) and diethanol amine (DEA), has been introduced and studied broadly (Abu-Zahra et al., 2007, Gray et al., 2008, Song et al., 2013). Even though studies showed efficient CO₂ capture, there are several drawbacks reported that need to be taken into account. The main drawbacks include corrosion problems due to corrosive property of ethanolamine solutions, high cost due to high energy consumption, degradation, high solvent volatility, and toxicity. Due to these drawbacks, ionic liquids were proposed (Anthony et al., 2004) but they have several limitations also as discussed in previous parts such as high cost and not ecologically advantageous. Deep eutectic solvents emerged recently as being free from most of these disadvantages (Marcus, 2019).

As a first quantitative study, Li et al. (2008) presented DESs as a potential CO₂ capturing method. The solubility of CO₂ in ChCl:urea DES was measured at different

temperatures, pressures, and molar ratios. Results showed solubility increases with increasing pressure and it decreases with increasing temperature. Different molar ratios didn't have a significant impact on solubility.

Mirza et al. (2015) performed experiments and modeling on three different DESs to analyze solubility of CO₂ at different temperatures and pressures. 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). From an experimental study observed Henry's constants were between the ranges of 3.7-6.1 MPa. Thermodynamic modeling was used to correlate experimental data and results showed good agreement with a 1.6% deviation.

Ali et al. (2016) examined different types of DESs for the feasibility of the CO₂ capturing process. The best performance was seen from methyltriphenylphosphonium bromide:monoethanol amine DES with the molar ratio of 1:6. Moreover, it was shown that 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. (2019) also investigated CO₂ capture by DESs. Results showed excellent CO₂ absorption capacity of DESs up to 1.00 mol CO₂/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 on the studied DESs.

4 TESTED DEEP EUTECTIC SOLVENTS IN EOR PROCESSES

In this part, the tested DESs in EOR processes will be introduced briefly, whereas detailed discussions will be done in the next chapter 5.

4.1 ChCl:Glycerol and ChCl:Urea DESs (a)

The first paper about the use of DESs for EOR was presented in March 2014 by Mohsenzadeh et al. at SPE EOR Conference in Muscat, Oman. In 2015 this paper was published to Journal of Petroleum Engineering and Science. Mohsenzadeh et al. (2014) investigated the application of two different kinds of DESs for heavy oil recovery enhancement. Those DESs are ChCl:Glycerol (1:2) (DES1) and ChCl:Urea (1:2) (DES2). DESs were mixed with formation brine to dilute them (50 vol%). Properties of heavy oil are 16 °API and 4200 cP viscosity at 25 °C. Properties of DESs are shown in table 4.1 for different temperatures.

**Tab. 4. 1: Properties of Studied DESs
(Source: Mohsenzadeh et al., 2014)**

Temperature (°C)		25	45	60	80
Density (gr/cm ³)	DES1(chcl:Glycerol)	1.2141	1.2028	1.1943	1.1829
	DES2 (chcl:Urea)	1.2185	1.2075	1.1945	1.1771
	50 vol.% DES1 with brine	1.145	1.132	1.123	1.107
	50 vol.% DES2 with brine	1.145	1.132	1.123	1.111
Viscosity (cp)	DES1 (chcl:Glycerol)	390	111	55	40
	DES2 (chcl:Urea)	250	63	34	14
	50 vol.% DES1 with brine	6.3	3.3	2.5	2.13
	50 vol.% DES2 with brine	3.8	3	2.5	2.0
PH	50 vol.% DES1 with brine	6.50	6.47	6.45	6.41
	50 vol.% DES2 with brine	9.70	9.57	9.07	8.48

Berea sandstone core samples were used for core flooding tests with a porosity of 18-20% and permeability of 12-32 mD at reservoir conditions (pressure=1200 psi and temperature=45°C, 60°C, 80°C). Emulsification, IFT change, wettability alteration, and oil recovery improvement were studied at different temperatures.

4.2 Choline Chloride (ChCl):Ethylene Glycol (EG) DES

Shuwa et al. (2014) also performed a similar study to Mohsenzadeh et al. (2014) but using a different type of DES. Shuwa et al. (2014) studied the effectiveness of ChCl:EG

(1:2) DES in heavy oil recovery at different temperatures. ChCl:EG mixture was diluted with brine at different concentrations between 0-100 vol%. With the increasing ratio of DES, density, and viscosity of DES+brine solution increases and it decreases with increasing temperature as shown in figure 4.1.

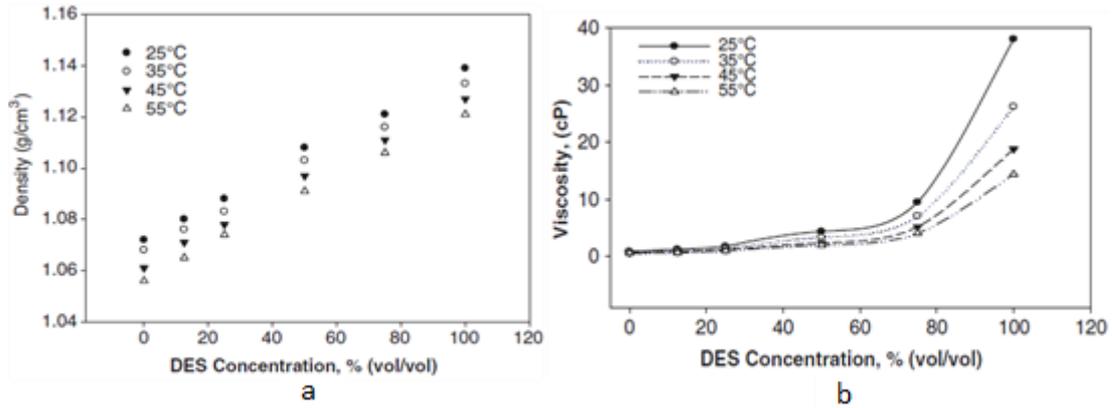


Fig. 4. 1: Variation of (a) Density and (b) Viscosity of DES Solution
(Source: Shuwa et al., 2014)

In the laboratory experiments, 50 vol% DES with brine was used. Heavy crude oil had 16 °API gravity and 4095 cP viscosity at 25 °C. After synthesis of DES and dilution with brine, this solution was used for the analysis of emulsification with oil, change of IFT between oil and solution, change of wettability, heavy oil recovery, and formation damage. For core flooding experiment Berea sandstone core plugs were used with porosity ranging between 17-20% and permeability of 13-62 mD at reservoir conditions (pressure=1200 psi and temperature=45°C, 60°C, 80°C).

4.3 ChCl:Glycerol and ChCl:Urea DESs (b)

Hadj-Kali et al. (2015) studied the potential application of two DESs (ChCl:Glycerol and ChCl:Urea) and their constituents (salt and HBD) as surfactants for EOR process. The molar ratio of DESs are 1:3 for ChCl:Glycerol (DES1) and 1:2 for ChCl:Urea (DES2). Densities of DES1 and DES2 are around 1.2 g/cm³ at 25°C. 10 wt% of NaCl was used to represent brine. Crude oil had properties of 12 cP viscosity and 0.886 specific gravity (28 °API). IFT measurements were carried out between oil and DES+brine solutions at atmospheric pressure, different temperatures, and different DES concentrations.

4.4 Choline Chloride (ChCl):Malonic Acid (MA) (1:1) and (2:1) (a)

Al-Weheibi et al. (2015) investigated the application of two different malonic acid-based DESs, namely ChCl:malonic acid with the molar ratios of (1:1) (DES1) and (2:1) (DES2). Al-Weheibi et al. (2015) presented this paper in March 2015 at the SPE EOR Conference in Manama, Bahrain. In 2019 this paper was published to international journal of oil, gas, and coal technology. These DESs were studied to see the effectiveness of enhancing heavy oil recovery after water flooding. Heavy crude oil had 16 °API gravity and 4095 cP viscosity at 25 °C.

Berea sandstone core samples were used which have 21% of average porosity and 230 mD of average permeability. DESs were diluted with formation brine (50 vol%) and also mixed with NaOH to decrease acidity (pH) from 1 to 5. DESs have high viscosities around 1500 cP at 20°C before mixing with NaOH. The densities of DESs at 20°C are as follows: 1.079 g/cm³ (DES1) and 1.092 g/cm³ (DES2). Both viscosity and density decrease with temperature. Stable emulsion formation, interfacial tension, wettability, oil recovery, and formation damage were studied at different temperatures to analyze the effectiveness of DESs. Core flooding test was performed at reservoir conditions (pressure=1200 psi and temperature=45°C, 60°C, 80°C).

4.5 Simulation Study of ChCl: MA (1:1) and (2:1) (b)

Al-Rujaibi et al. (2016) conducted a simulation study to analyze the heavy oil enhancement due to wettability change by using DESs. Studied DESs are ChCl:MA with two different molar ratios, (1:1) (DES1) and (2:1) (DES2). For simulation works, Al-Rujaibi et al. (2016) used the experimental works of Al-Weheibi et al. (2015) to model all core flooding tests. Al-Weheibi et al. (2015) performed experimental analyzes for the same types of DESs. Average porosity and permeability are 21% and 205 mD, respectively. Al-Rujaibi et al. (2016) used ECLIPSE 100 black oil simulator for the simulation study. Wettability alterations were investigated based on relative permeability curves and oil recovery enhancement due to DES injection was evaluated.

4.6 Sequential DESs (ChCl:Glycerol and ChCl:Urea) and Steam Injection

Mohsenzadeh et al. (2017) investigated the effectiveness of DESs injection, steam injection, and their combinations to enhance heavy oil recovery. Two types of DESs were used in this study, namely ChCl:Glycerol (1:2) (DES1) and ChCl:Urea (1:2) (DES2) were injected with different concentrations at reservoir conditions. After DES injection, steam injection experiments were performed at high pressure and temperature. Results obtained from DES flooding followed by steam flooding were compared with the results of steam flooding alone. Table 4.2 shows heavy oil and brine properties. Properties of DESs are shown in table 4.3.

**Tab. 4. 2: Heavy Crude Oil and Brine Properties
(Source: Mohsenzadeh et al., 2017)**

Oil properties							Brine properties	
Chemical properties			Physical properties				Density @ 25 °C	1.05 g/cm ³
Molecular weight, g/mol	519	Temperature, °C	Viscosity, cP	Density, g/cm ³	Specific gravity, SG	°API	Total salinity	7.7 wt.%
Total acid no., mgKOH/mg	1.82	25	10,970	0.965	0.968	14.68	Sodium	25,083 kg/m ³
Sulphur content, wt.%	2.680	30	9713	0.961	0.965	15.13	Calcium	3.672 kg/m ³
Asphaltene content, wt.%	1.6	40	5851	0.951	0.960	15.90	Magnesium	0.878 kg/m ³
Total nitrogen, mg/kg	1948	45	2350	0.941	0.957	16.36	Iron	0.045 kg/m ³
Total salt, lbs/1000 bbls	11.0	60	1086	0.934	0.956	16.51	Chloride	47.722 kg/m ³
Characterization factor, UOP375	70	540	-	-	-	-	Sulphate	0.247 kg/m ³
	80	330	-	-	-	-	Bicarbonate	0.079 kg/m ³
							Filtration unit	0.45 µm

**Tab. 4. 3: Properties of DES Solutions
(Source: Mohsenzadeh et al., 2017)**

Solution	Mol.% of DES	Wt.% of DES	pH @ 45 °C	Density @ 45 °C, g/cm ³	Viscosity @ 45 °C, cP
Formation brine	0	0	7.450	1.0503	0.8
Undiluted DES1	100	100	6.304	1.2028	130.1
2-fold diluted DES1	21.1	51.5	6.470	1.1320	6.3
20-fold diluted DES1	0.75	5.7	7.126	1.0632	1.6
Undiluted DES2	100	100	10.991	1.2075	87.5
2-fold diluted DES2	17.2	51.5	9.828	1.1435	5.9
20-fold diluted DES2	0.93	5.7	8.696	1.0702	1.3

The high thermal stability of DESs was the main motivation for authors to conduct such kind of experimental study. High thermal stability of DES1 and DES2 were verified after performing thermogravimetric analysis. As shown in figure 4.2, both DESs started to decompose at around 200 °C. Results showed 320 °C of maximum decomposition temperature for DES1 and 370 °C for DES2.

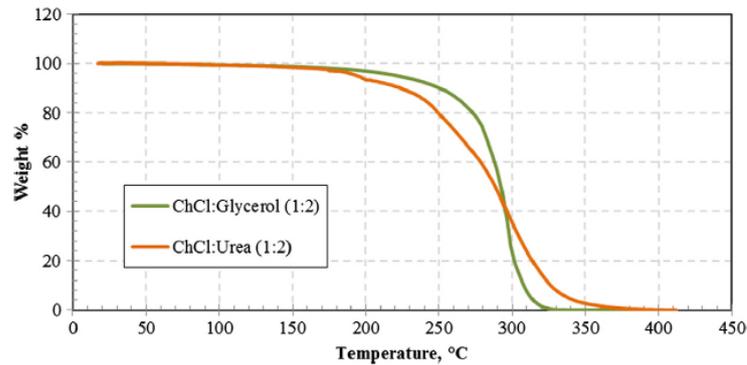


Fig. 4. 2: Thermogravimetric Analysis of DES1 and DES2
(Source: Mohsenzadeh et al., 2017)

4.7 Choline Chloride-based DESs for Secondary Water Flooding

El-hoshoudy et al. (2019) experimentally and theoretically investigated four ChCl-based DESs for secondary water flooding. Four DESs used in this study are ChCl:urea (1:2) (DES1), ChCl:thio urea (1:2) (DES2), ChCl:ethylene glycol (1:2) (DES3), ChCl:glycerol (1:2) (DES4). Properties of DESs are reported in table 4.4.

Tab. 4. 4: Properties of Tested DESs
(Source: El-hoshoudy et al., 2019)

DES	composition	Density (ρ) kg/m ³	Kinematic viscosity (η) m ² /s \times 10 ⁻⁶ at 373 K	Molar mass (M_m) g/mol	Melting point (T_m) K	Fusion temperature (T_{fus}) K	Surface tension (σ) mN m ⁻¹	Conductivity (κ) mS/cm
DES ₁	(Chcl: U)	1170	89.0	240.67	407.15	285.15	52	0.75
DES ₂	(Chcl: TU)	1230	177.0	272.79	448.15	342.15	58	N/a
DES ₃	(Chcl: EG)	1120	93.0	248.72	260.25	207.15	49	7.61
DES ₄	(Chcl: G)	1180	81.7	308.78	290.95	233.15	55.8	1.05

Flooding experiments were performed on a linear sandpack and then simulated using CMG software. El-hoshoudy et al. (2019) measured thermal degradation and DESs showed thermal stability as shown in figure 4.3.

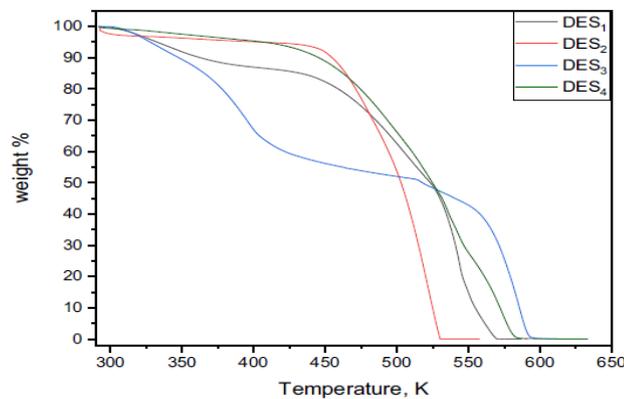


Fig. 4. 3: Thermal Stability Analysis of DESs
(Source: El-hoshoudy et al., 2019)

Figure 4.3 indicates that the highest thermal stability achieved with DES2. DES3 showed the lowest thermal stability due to the high volatility of ethylene glycol (El-hoshoudy et al., 2019)

4.8 Performance of DESs for Oil Enhancement from Tight Sands

Huang et al. (2020) studied the effects of different novel chemical agents including eight different house-made DESs for oil recovery enhancement from tight sands after fracturing via spontaneous imbibition. Tight sandstone core samples have an average porosity of 7% and 0.1 mD of average permeability. Oil has a density of 880 kg/m³ and viscosity of 11 cP at 25 °C and atmospheric pressure. Different DESs used in this study are summarized in table 4.5. IFT between light crude oil and DES solutions and also oil recovery were measured at different concentrations.

Tab. 4. 5: List of Tested DES Solutions
(Source: Huang et al., 2020)

Name/label	Composition
DES3	Sodium carbonate and glycerin (1:2 molar ratio)
DES4	Sodium carbonate and urea (1:2 molar ratio)
DES5	Choline chloride and sodium carbonate (1:1 molar ratio)
DES6	<i>N, N</i> -bis (2-[bis(carboxymethyl)amino]ethyl) glycine and dodecylbenzenesulfonic acid (1:10 molar ratio)
DES7	Choline chloride and dodecylbenzenesulfonic acid (1:1 molar ratio)
DES9	Sodium carbonate and sodium sulfate (1:2 molar ratio)
DES11	Sodium carbonate and 1-butyl-3-methylimidazolium tetrafluoroborate (5:1 molar ratio)
DES14	Choline chloride and sodium carbonate (1:2 molar ratio)

5 RESULTS & DISCUSSIONS ON PERFORMANCE OF DESs IN EOR PROCESSES

5.1 Stable Emulsion Formation

ChCl:Glycerol (DES1) and ChCl:Urea (DES2) (a)

Mohsenzadeh et al. (2014) showed no stable emulsion formation between DES solution and oil in their studies for DES1 and also for DES2. Results are shown in figure 5.1 for each DESs before, directly after, and 1 day after mixing with different concentrations (from 50% to 1%). It was observed DES solution and oil are separated from each other.

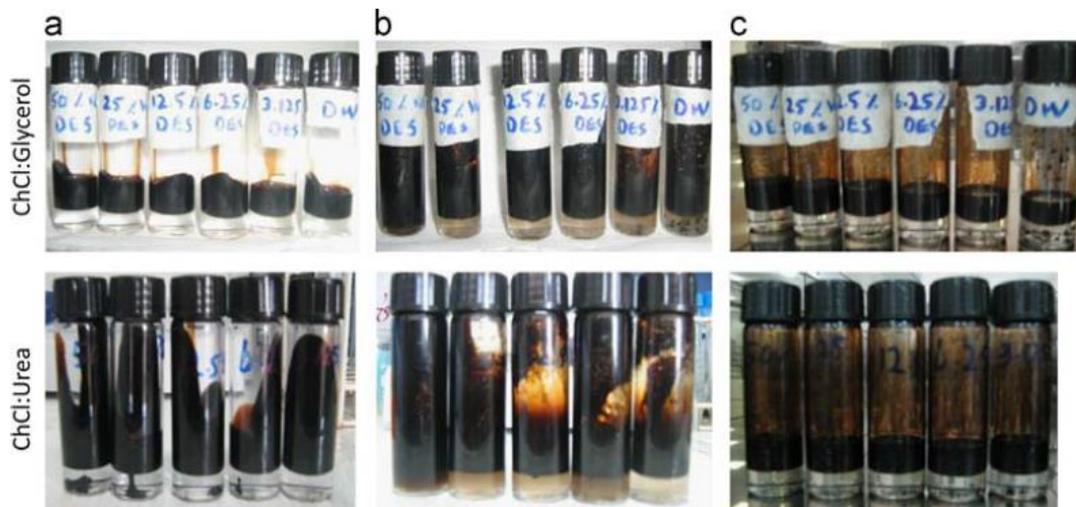


Fig. 5. 1: Emulsification of DESs and Heavy Oil (a) before (b) directly after and (c) one day after mixing (Source: Mohsenzadeh et al., 2014)

Choline Chloride (ChCl):Ethylene Glycol (EG) DES (a)

Similarly to Mohsenzadeh et al. (2014), Shuwa et al. (2014) also observed no stable emulsion formation between oil and DES (ChCl:EG) solution. Oil stayed at the top and the DES+brine solution stayed at the bottom part of the tube.

Choline Chloride (ChCl):Malonic Acid (MA) (1:1) and (2:1) (a)

Al-Weheibi et al. (2015) showed the results of the emulsification test as shown in figure 5.2.

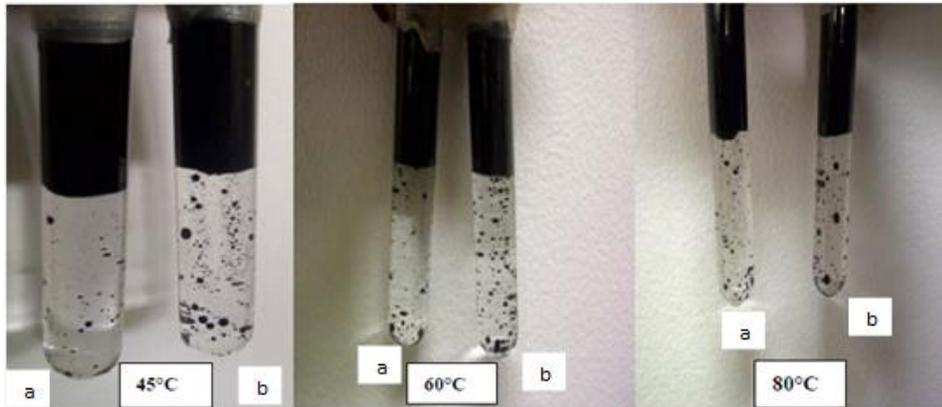


Fig. 5. 2: Mixture of Oil with (a) ChCl:MA (1:1) and (b) ChCl:MA (2:1)
(Source: Al-Weheibi et al., 2015)

From figure 5.2 we can see heavy oil and DES+brine mixtures are separated from each other after mixing and aging for 1 day. Oil is at the top part and the DES+brine solution is at the bottom part. There is only a limited emulsion formation. There were not any significant changes were observed by increasing or decreasing temperature. Moreover, for all temperatures, no precipitations were observed (Al-Weheibi et al., 2015).

5.2 Interfacial Tension (IFT) Change

ChCl:Glycerol (DES1) and ChCl:Urea (DES2) (a)

Mohsenzadeh et al. (2014) reported interfacial tension measurement results between oil/brine, oil/DES1, and oil/DES2 solutions at different temperatures as shown in figure 5.3.

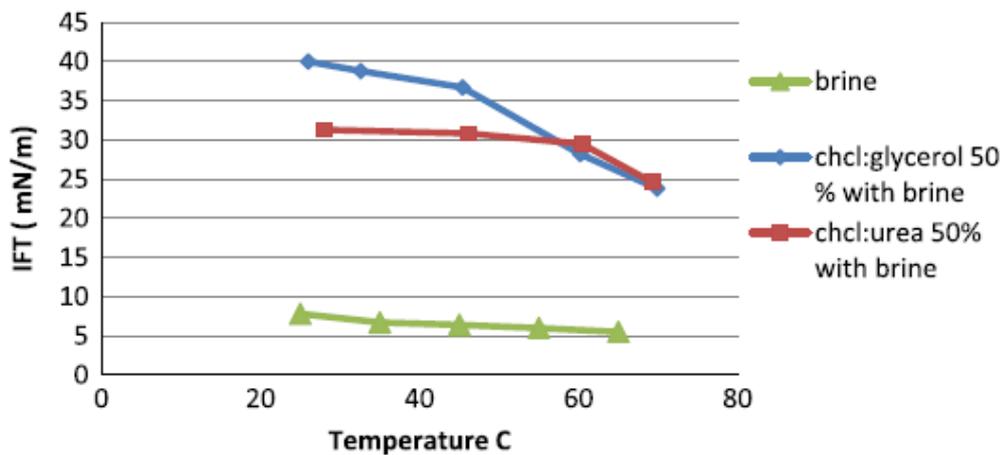


Fig. 5. 3: IFT Values between Oil/Brine and Oil/DESs
(Source: Mohsenzadeh et al., 2014)

From the figure, we can see the decrease of IFT with increasing temperature. However, a significant increase of IFT rather than decrease can be observed when DES is mixed with brine. IFT of oil/DES solution is much higher compared to oil/brine. Authors believe the main reasons for this must be weaker interaction between functional groups of DES and functional groups of oil. Due to van der Waals force, functional groups of DES must have had a lower attraction with functional groups of oil which resulted in an increase of IFT. Functional groups of DES are: $-OH$ for DES1; $-NH_2$, $CO-$ for DES2, and functional groups of oil are asphaltenes and resins represented by carboxylate groups. Moreover, larger cations are present in DES such as choline ions. This might lead to an increase of IFT due to stronger coulombic attraction forces.

Choline Chloride (ChCl):Ethylene Glycol (EG) DES (a)

Shuwa et al. (2014) reported the comparison of IFT between oil/brine and oil/DES solution and their variation with temperature as shown in figure 5.4. DES concentration is 50 vol%.

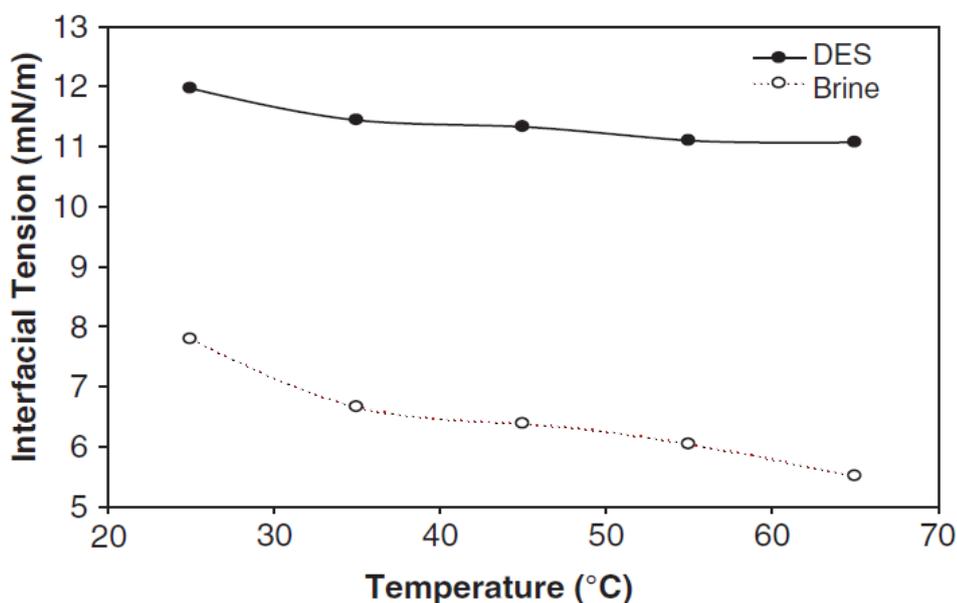


Fig. 5. 4: IFT Values for Brine and DES and Variation with Temperature
(Source: Shuwa et al., 2014)

Shuwa et al. (2014) also observed a decrease of IFT with temperature and an increase of IFT for DES+brine solution. The reasons for the increase of IFT were explained as due to van der Waals forces (interactions between functional groups of oil and DES solution) and coulombic forces (presence of larger cations in DES).

ChCl:Glycerol and ChCh:Urea DESs (b)

Unlike Mohsenzadeh et al. (2014), the results of Hadj-Kali et al. (2015) showed DESs significantly reduces IFT between oil and DESs solutions. This is important for the enhancement of oil recovery. Figure 5.5 shows the variation of IFT with ChCl:glycerol (1:3) (DES1) concentration and temperature.

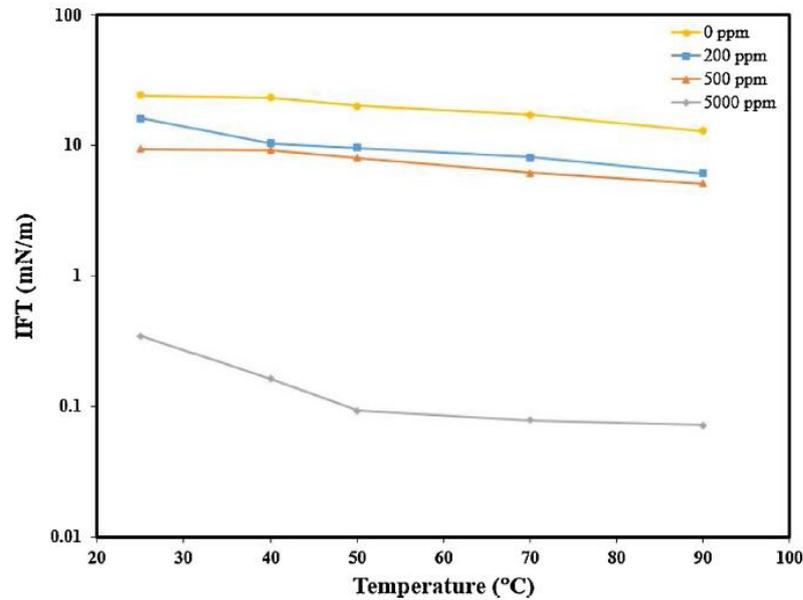


Fig. 5. 5: Variation of IFT with Concentration of DES1 and Temperature (Source: Hadj-Kali et al., 2015)

From the figure, we can see IFT reduction with increasing DES1 concentration. At 25 °C, when the concentration of DES1 is 0 ppm (brine alone), IFT between oil and brine is 24.1 mN/m. When DES1 concentration was increased to 5000 ppm, IFT decreased to 0.35 mN/m at 25 °C. This value reduced even more down to 0.072 mN/m with increasing temperature.

To see the effects of the constituents of DESs on IFT reduction, Hadj-Kali et al. (2015) analyzed the addition of choline chloride and glycerol separately without forming a eutectic mixture. Figure 5.6 shows the results for DES1.

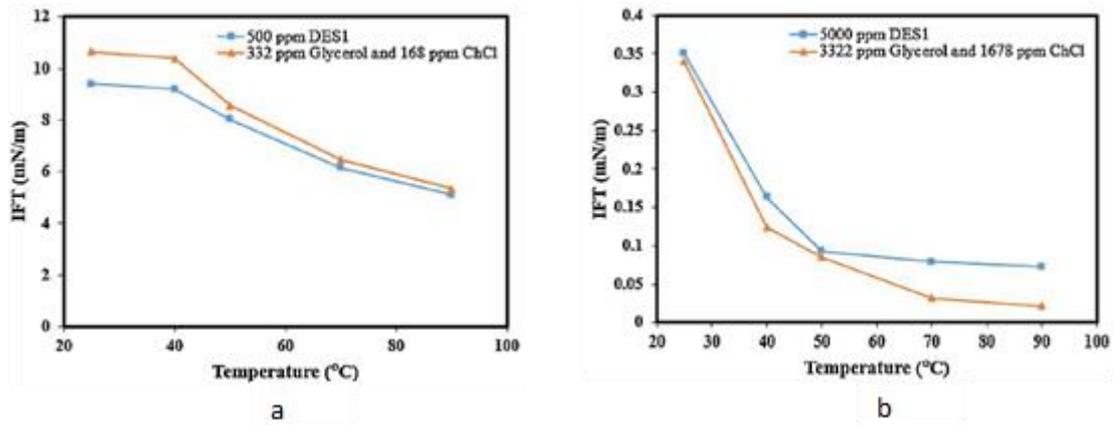


Fig. 5. 6: IFT of DES1 and Its Constituents at (a) Low and (b) High Concentrations (Source: Hadj-Kali et al., 2015)

From the figure, we can observe there is not much difference between DES1 and its constituents (ChCl and glycerol) in terms of IFT reduction. At lower concentration DES1 yields lower IFT value compared to its components. Nevertheless, individual constituents yield lower values of IFT at higher concentrations.

The same test was conducted for ChCl:urea (DES2) solution as well but only for 5000 ppm concentration. Figure 5.7 shows the results.

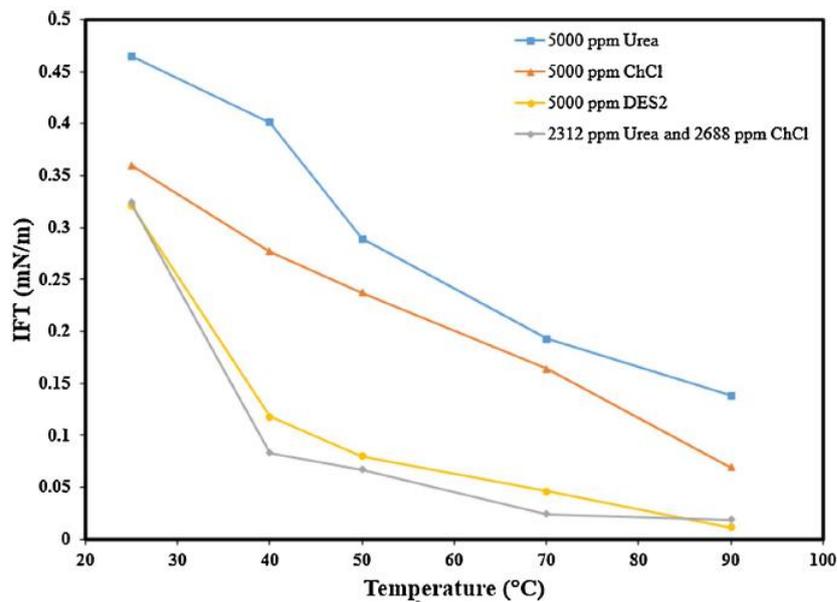


Fig. 5. 7: Effects of DES2 and Its Constituents to IFT (Source: Hadj-Kali et al., 2015)

Again here for DES2 also we can see approximately similar IFT reduction using DES2 or using its mixed components (ChCl:urea). However, when one of the

components of DES2 used alone, IFT reduction is not as low as it is observed with DES2.

Moreover, tests were performed for different concentrations of DESs and its components to identify optimum concentration. Results showed 3000 ppm as an optimum value. Above this value negligible decrease of IFT was observed. The authors concluded that DESs have the ability to decrease IFT drastically. This contradicts the results of Mohsenzadeh et al. (2014) in which Mohsenzadeh et al. (2014) used the same DESs but with a much higher concentration (50 vol%) and different oil (heavy oil). Hadj-Kali et al. (2015) commented on the concentrations of DESs which Mohsenzadeh et al. (2014) used is too high. All the concentrations used in Hadj-Kali et al. (2015) work is lower than this value. To compare with their work, Hadj-Kali et al. (2015) presented IFT values with those high concentrations as it is shown in table 5.1.

Tab. 5. 1: IFT Values (mN/m) of DES2 at various concentrations and temperatures (Source: Hadj-Kali et al., 2015)

	Temperature (°C)				
	25	40	50	70	90
Pure DES2	0.259 ₁	0.106 ₂	0.233 ₁	0.084 ₁	0.006 ₁
50% DES2 and 50% Brine	0.260 ₃	0.111 ₁	0.095 ₀	0.041 ₁	0.006 ₁
25% DES2 and 75% Brine	0.262 ₂	0.111 ₁	0.095 ₁	0.042 ₀	0.006 ₄

As can be seen from the table for all displayed concentrations IFT was reduced drastically and for DES concentrations after 25% there is only a slight decrease of IFT.

Choline Chloride (ChCl):Malonic Acid (MA) (1:1) and (2:1) (a)

Al-Weheibi et al. (2015) reported the results of IFT measurement between oil/brine, oil/ChCl:MA (1:1) (DES1), and oil/ChCl:MA (2:1) (DES2) as shown in table 5.2.

Tab. 5. 2: IFT Values between Oil-Brine and Oil-DESs at Different Temperatures (Source: Al-Weheibi et al., 2015)

<i>Oil-brine</i>		<i>Oil-DES1</i>		<i>Oil-DES2</i>	
<i>Temp. °C</i>	<i>IFT (mNm⁻¹)</i>	<i>Temp. °C</i>	<i>IFT (mNm⁻¹)</i>	<i>Temp. °C</i>	<i>IFT (mNm⁻¹)</i>
25	7.8	45	21.92	45	21.88
35	6.7	60	19.09	60	19.73
45	6.4	80	8.31	80	9.80
55	6				
65	5.5				

We can see from the table that IFT values decrease with increasing temperature for all cases due to the reduction of intermolecular forces between interfaces. When we compare IFT values between oil/brine and oil/DES, oil/DES IFT is significantly higher than oil/brine. This shows the addition of DES resulted in an increase of IFT instead of decreasing. One of the indications for this is only limited emulsion formation as discussed in the previous part. Other main reasons are explained as due to van der Waals forces and coulombic forces.

ChCl:Urea (DES1), ChCl:Thio urea (DES2), ChCl:Ethylene Glycol (DES3), ChCl:Glycerol (DES4)

El-hoshoudy et al. (2019) reported the surface and interfacial tension measurement results between oil/brine and oil/DES solutions (50 vol %) at 313.15 K in figure 5.8.

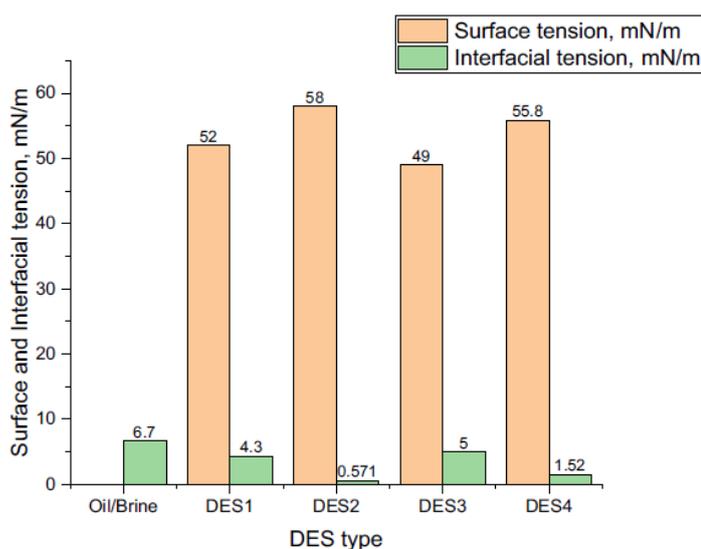


Fig. 5. 8: Surface and Interfacial Tension Values between Oil/Brine and Oil/DESs (Source: El-hoshoudy et al., 2019)

Oil/brine showed an IFT value of 6.7 mN/m. Reduction in IFT was observed for all DES solutions. DES2 showed the highest IFT reduction. However, the highest surface tension was seen in DES2 also. The authors believe this is because of an increase of cohesive forces due to the intensity of a hydrogen bond.

C₁₀H₁₉N₃O₆ : C₁₈H₃₀O₃S (1:10) (DES6) and ChCl:Na₂CO₃ (1:2) (DES14)

Huang et al. (2020) performed IFT measurements between light crude oil and various chemicals, including DES6 and DES14 at different concentrations. The results are shown in figure 5.9.

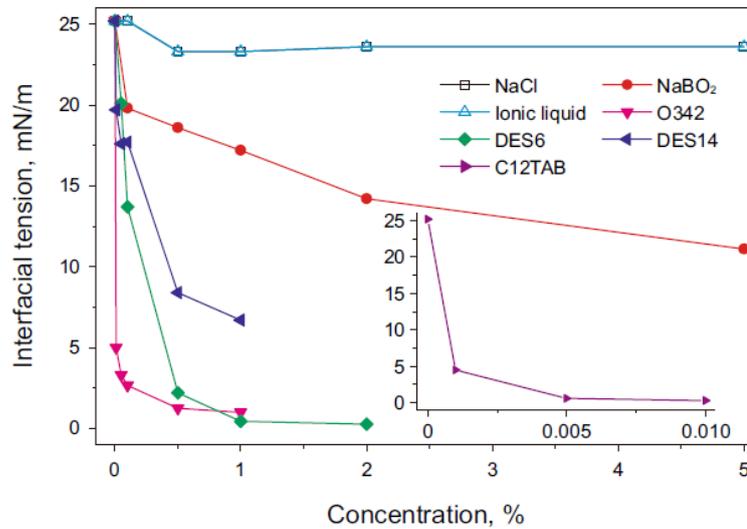


Fig. 5. 9: Effects of Various Chemicals on IFT Including DES6 and DES14 (Source: Huang et al., 2020)

It can be witnessed in figure 5.9 that both DESs showed significant IFT reduction. By comparing two DESs, better performance was observed with DES6 compared to DES14. Considering 1% concentration IFT reduction due to DES14 is from 25 mN/m to 7 mN/m, whereas this value is from 25 mN/m down to 1.5 mN/m with DES6.

5.3 Wettability Alteration

ChCl:Glycerol (DES1) and ChCl:Urea (DES2) (a)

Results of Mohsenzadeh et al. (2014) showed the two studied DESs were able to change wettability towards intermediate air-wetting from the liquid wetting condition in the rock-oil-air system. The contact angle of 28° was obtained when the rock sample was treated with formation brine as a reference for 14 days. With the treatment of ChCl:Glycerol solution for 14 days, the contact angle increased from 28° to 42° . ChCl:Urea solution resulted in an even higher increase in contact angle from 28° to 52° for the same period of time. The results are shown in figure 5.10.



Fig. 5. 10: Contact angle Measurements with Brine and DES Solutions (Source: Mohsenzadeh et al., 2014)

Choline Chloride (ChCl):Ethylene Glycol (EG) DES (a)

Shuwa et al. (2014) analyzed the wettability alteration with spontaneous imbibition test in Amott cell using DES and brine. Wettability plays the main role in affecting spontaneous imbibition (Sheng, 2017, Huang et al., 2020). Figure 5.11 shows the effect of the DES+brine solution on oil recovery enhancement as a consequence of wettability alteration at 45°C, 60°C and 80°C.

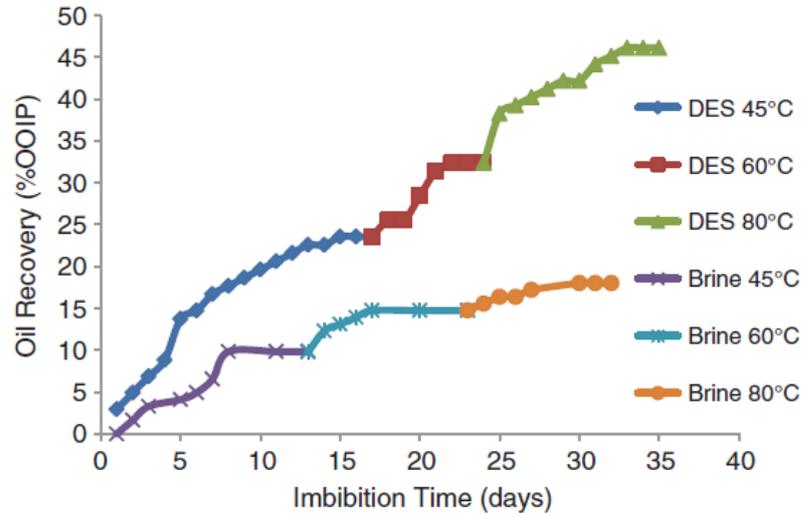


Fig. 5. 11: Oil Recovery by Brine and DES+Brine Solution
(Source: Shuwa et al., 2014)

From the figure, it can be seen that the DES+brine solution increases oil recovery significantly for all temperature values. Oil recovery with brine alone is 10% at 45°C, 15% at 60°C and 18% at 80°C. When 50 vol% ChCl:EG DES is mixed with brine, this value increases up to 24% at 45°C, 33% at 60°C and 47% at 80°C. By comparing oil recovery by brine and DES, an additional 14%, 18%, and 29% of oil recovered due to the addition of DES at 45°C, 60°C and 80°C, respectively. This shows that the addition of DES reduces oil wetting capability.

Choline Chloride (ChCl):Malonic Acid (MA) (1:1) and (2:1) (a)

Al-Weheibi et al. (2015) investigated wettability alteration by contact angle measurement and also by spontaneous imbibition tests in amott cell. The results of contact angle measurements are shown in figure 5.12.

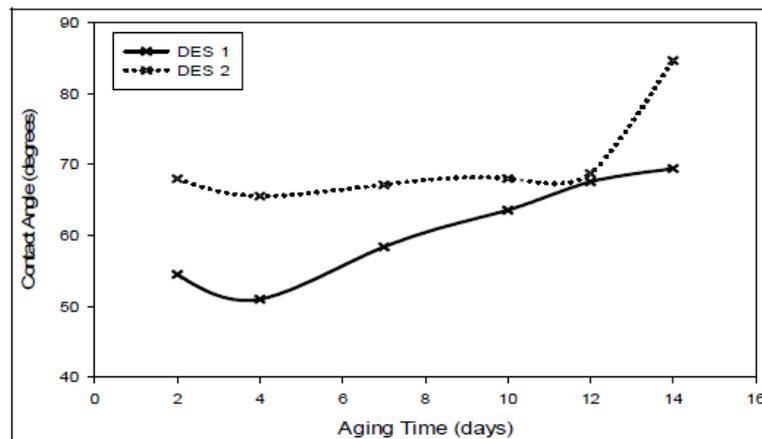


Fig. 5.12: Effects of DES1 and DES2 for Contact Angle Increment (Source: Al-Weheibi et al., 2015)

DESs result in a significant increase in contact angle between oil/DES solutions which changed wettability towards less oil-wet conditions with increasing aging time. For DES2 it increases up to 85° and for DES1 up to 69°. The increment is more severe in DES2. The authors explained this due to the presence of a high amount of choline in DES2 (2:1) compared to DES1 (1:1). The high amount of choline gives a more positive charge and this makes the oil surface more positive.

Moreover, Al-Weheibi et al. (2015) showed spontaneous imbibition test results which gave an indication of wettability alteration. The addition of DES into brine significantly increased oil recovery as shown in figure 5.13.

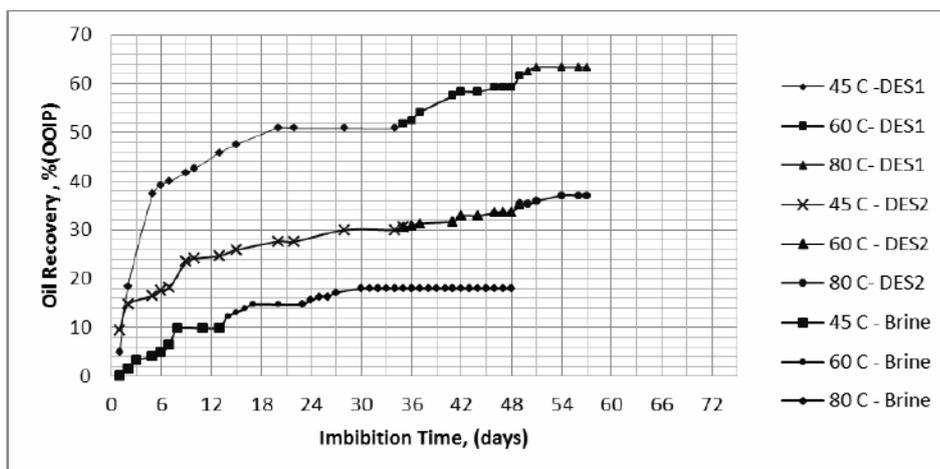


Fig. 5.13: Oil Recovery by Spontaneous Imbibition using Brine, DES Solutions (Source: Al-Weheibi et al., 2015)

DES1 solution showed the highest oil recovery compared to the brine and DES2 solution. We can also see for all cases recovery increases with increasing temperature. At 80°C total oil recoveries are 18% for brine, 33% for DES2, and 63% for DES1. Authors stated the main reason for observation of wettability alteration is due to the interaction of DESs with rock material which increases recovery.

Choline Chloride (ChCl):Malonic Acid (MA) (1:1) (DES1) and (2:1) (DES2) (b)

Al-Rujaibi et al. (2016) performed history matching between experimental and simulation data for oil recovery of brine, DES1, and DES2 at 45 °C, 60 °C and 80 °C. Figure 5.14 shows results for 45 °C.

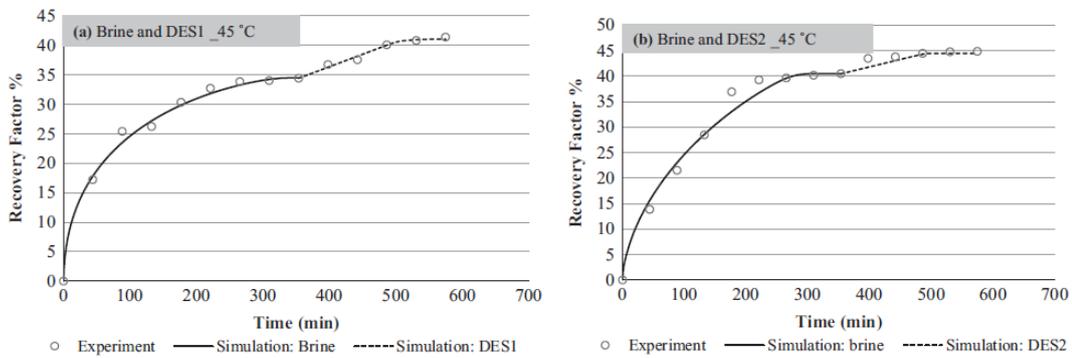


Fig. 5. 14: Experimental and Simulated Oil Recovery for Brine and DESs at 45°C (Source: Al-Rujaibi et al., 2016)

From history matching, relative permeability parameters were obtained. The effectiveness of DES injection on wettability alteration and heavy oil enhancement were analyzed by the interpretation of relative permeability curves. Figure 5.15 shows oil-water relative permeability curves for brine and DES1 at different temperatures and figure 5.16 for brine and DES2.

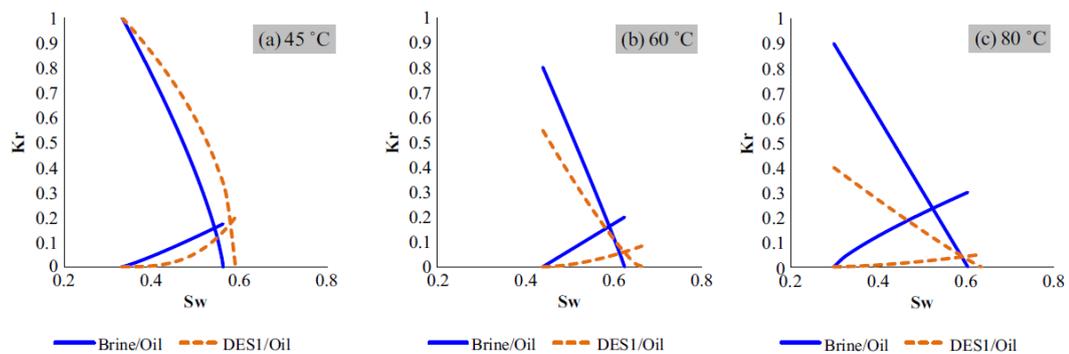


Fig. 5. 15: Oil-Water Relative Permeability Curves for Brine and DES1 (Source: Al-Rujaibi et al., 2016)

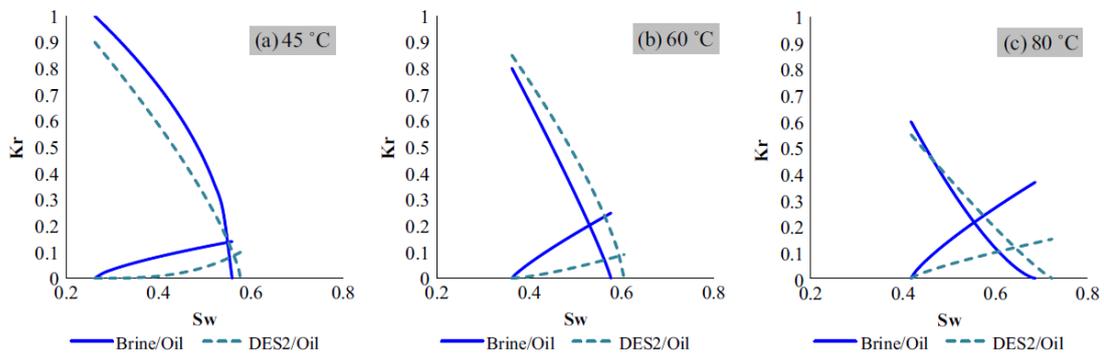


Fig. 5. 16: Oil-Water Relative Permeability Curves for Brine and DES2 (Source: Al-Rujaibi et al., 2016)

From results, it can be observed transformed endpoints and shift in relative permeability crossover points are indications of wettability alteration due to DESs injection. Moreover, temperature showed a significant impact. Figure 5.17 shows the comparison of DES1 and DES2 at different temperatures.

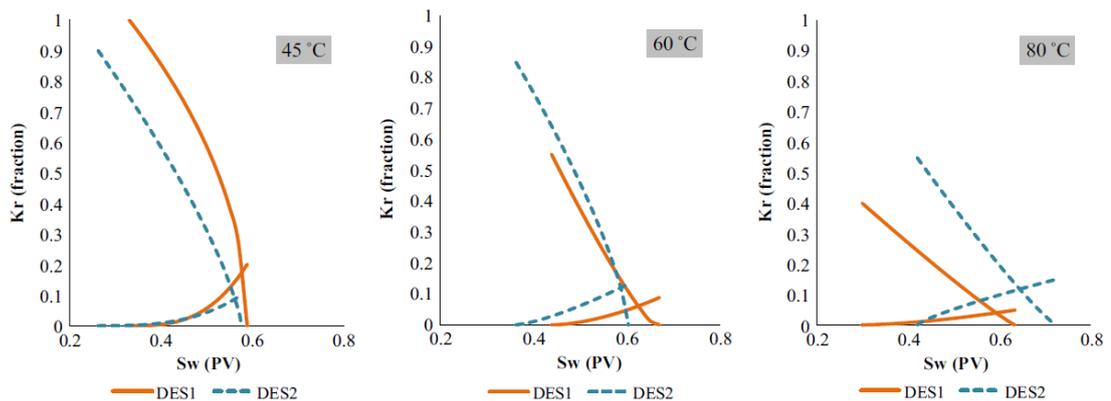


Fig. 5. 17: Effect of Temperature on Relative permeability Curves (Source: Al-Rujaibi et al., 2016)

DES1 showed better performance at 45°C because oil relative permeability is higher at any saturation compared to DES2. In addition, the saturation crossover point of DES1 (58%) is higher than DES2 (57%). However, DES2 showed better performance at 80°C. Oil relative permeability of DES2 is higher than DES1 and also saturation crossover point of DES2 (65%) is higher compared to DES1 (59%).

Wettability alterations can be analyzed also by interpretation of relative permeability ratio curves (k_{rw}/k_{ro}). Shifts to right are an indication of wettability alteration towards more water-wet conditions (Al-Rujaibi et al., 2016). Figure 5.18 and 5.19 show relative permeability ratio curves for brine, DES1, and DES2 at different temperatures.

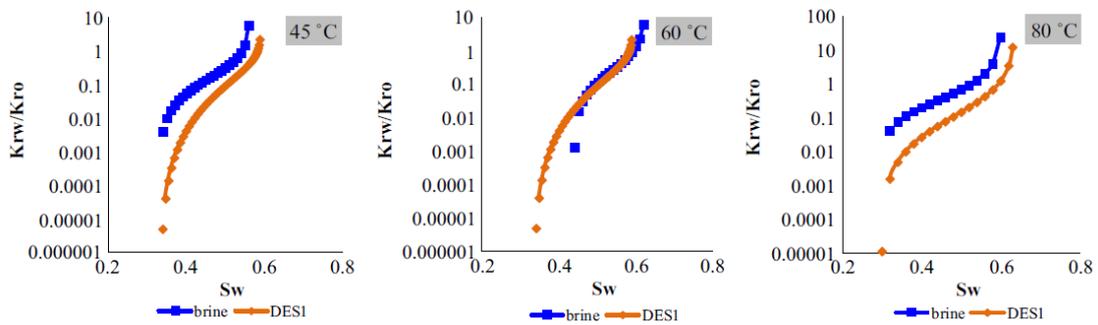


Fig. 5. 18: Relative Permeability Ratio Plots for Brine and DES1
(Source: Al-Rujaibi et al., 2016)

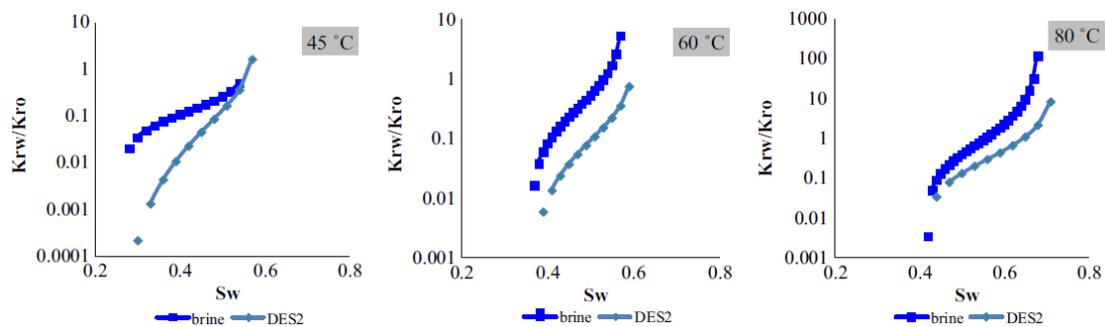


Fig. 5. 19: Relative Permeability Ratio Plots for Brine and DES2
(Source: Al-Rujaibi et al., 2016)

Figures indicate the shift of k_{rw}/k_{ro} to the right which is an indication of wettability change towards the more water-wet condition. Moreover, k_{rw}/k_{ro} ratio is lower for DES injection compared to brine injection at any saturation. This shows the improvement in oil relative permeability (k_{ro}) with DES injection.

ChCl:Urea (DES1), ChCl:Thio urea (DES2), ChCl:Ethylene Glycol (DES3), ChCl:Glycerol (DES4)

El-hoshoudy et al. (2019) measured DES adsorption to sandstone formation at different concentrations to analyze the wettability change. The results are shown in figure 5.20.

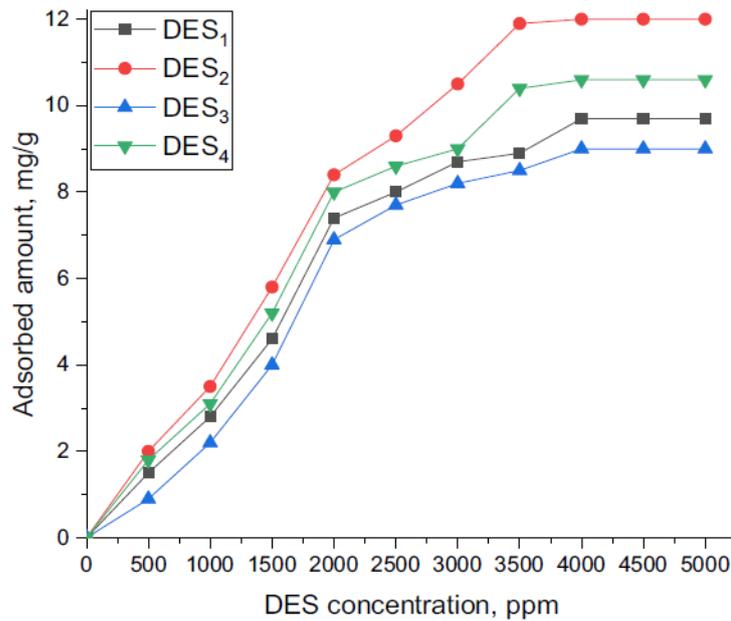


Fig. 5. 20: Adsorption of DESs at Different Concentrations
(Source: El-hoshoudy et al., 2019)

DESs adsorption increases with increasing concentration until they reach constant value at around 3600 ppm. DES2 showed the highest adsorption value. ChCl-based salts are positively charged and outer layers of sandstone reservoirs are negatively charged, so this leads to the adsorption of positively charged ChCl-based salts (El-hoshoudy et al., 2019). Due to electrostatic forces, this adsorption process changes wettability towards more water-wet and leads to an increase in oil recovery (El-hoshoudy et al., 2019).

5.4 Oil Recovery Improvement

ChCl:Glycerol (DES1) and ChCl:Urea (DES2) (a)

Results of core flooding experiments of Mohsenzadeh et al. (2014) showed a significant increase in oil recovery at different temperatures. Figure 5.21 shows total oil recovery values by brine flooding followed by ChCl:glycerol solution injection at 45°C, 60°C and 80°C. Recovery values are shown in the percentage of initial oil in place (%IOIP).

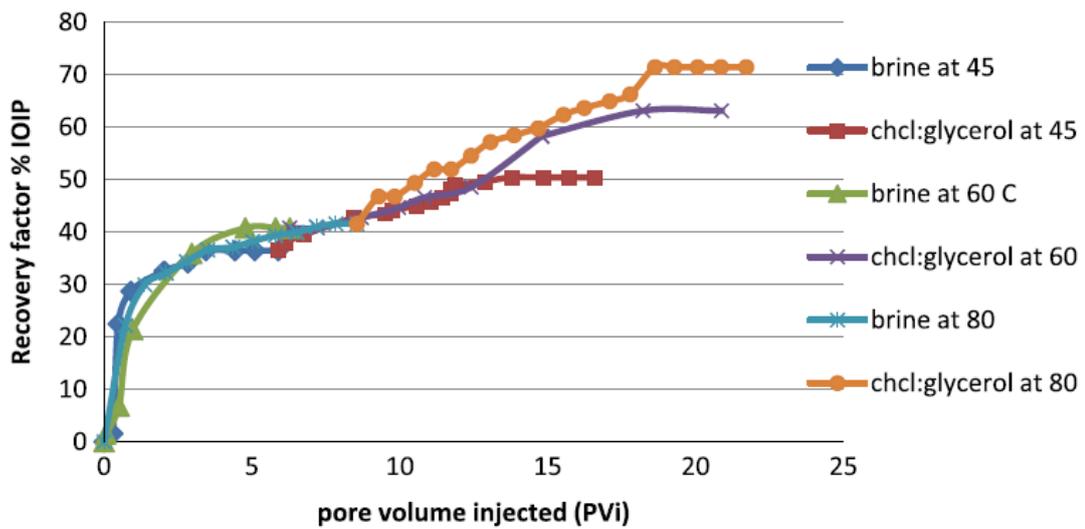


Fig. 5. 21: Oil Recovery by Brine and ChCl:Glycerol Solution
(Source: Mohsenzadeh et al., 2014)

From the figure, it can be observed that with increasing temperature oil recovery also increases. Oil recovery after brine flooding is 36.4% at 45°C, 40.7% at 60°C and 41.6% at 80°C. ChCl:glycerol solution injection resulted in an increase of additional oil recovery by 14%, 22.3%, and 29.8% at 45°C, 60°C and 80°C, respectively. Figure 5.22 shows total oil recovery values by brine flooding and ChCl:urea solution injection. Additional oil recovery by injection of ChCl:urea solution is 23.2% at 45°C, 30.8% at 60°C and 26.3% at 80°C.

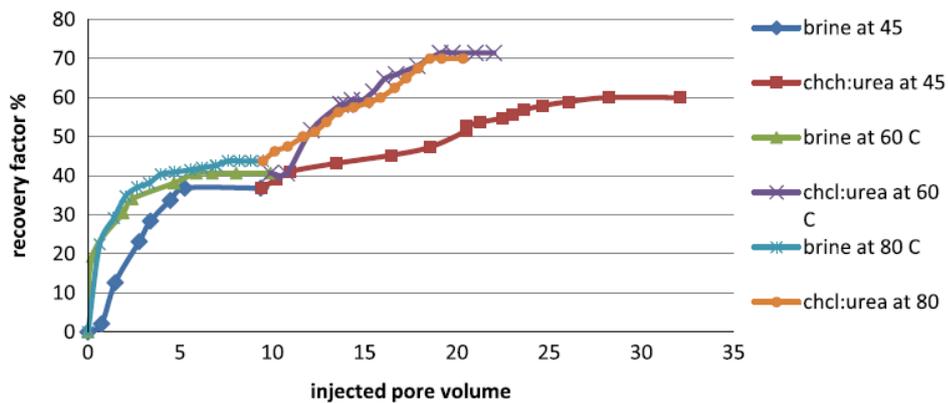


Fig. 5. 22: Oil Recovery by Brine and ChCl:Urea Solution
(Source: Mohsenzadeh et al., 2014)

ChCl:Urea showed better performance compared to ChCl:Glycerol solution due to its higher alkalinity. Since no stable emulsion formation and no IFT reduction observed in this type of DES injection, viscous forces and wettability alteration are the main factors

Oil saturation	S_o (after brine recovery)	39.6%	37.4%	44%	31%	42%	41%
	S_o (after extra recovery)	34.2%	32.8%	39%	27%	39%	38%
Oil recovery factor % based on ROIP	Brine flooding	43.5%	33.3%	34.43%	46.00%	33.93%	43.85%
	DES flooding	13.57%	12.29%	10.0%	10.3%	8%	7.3%
Oil recovery factor % based on OOIP	Brine flooding	43.5%	33.3%	34.43%	46.00%	33.9%	43.85%
	DES flooding	8.2%	7.7%	6.6%	8%	5.4%	4.1%

After brine flooding additional oil recoveries by DES1 solution are 6.6%, 7.7%, and 8.2% (OOIP) at 45°C, 60°C and 80°C, respectively. For DES2 solution these values are 4.1%, 5.4%, and 8% (OOIP) at the same temperatures.

Choline Chloride (ChCl):Malonic Acid (MA) (1:1) and (2:1) (b)

Mobility ratio results of Al-Rujaibi et al. (2016) showed a decrease in mobility ratio due to ChCl:MA (1:1) (DES1) and ChCl:MA (2:1) (DES2) injection. This leads to an increase in sweep efficiency and oil recovery enhancement. Figure 5.24 shows the results of the mobility ratio measurement.

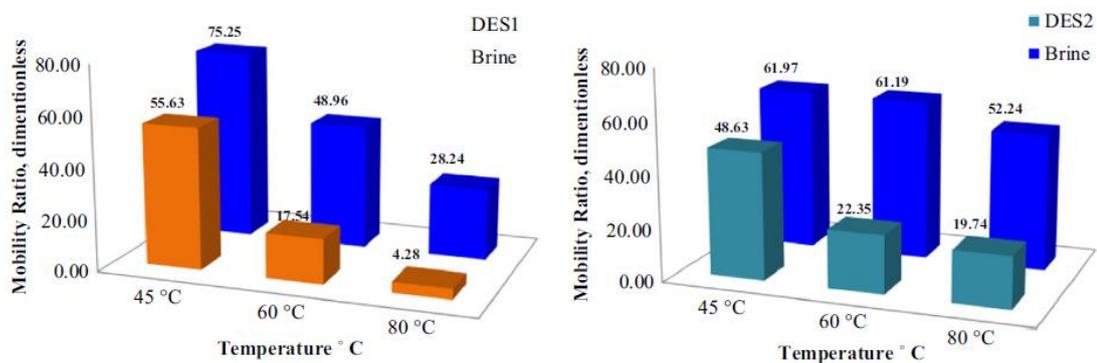


Fig. 5. 24: Mobility Ratio of Brine, DES1, and DES2 (Source: Al-Rujaibi et al., 2016)

Simulation studies were performed to investigate the oil recovery due to brine and DES injections at different temperatures. 30 years of injection were considered. 20 years of water flooding followed by 10 years of DES injection as a tertiary stage was found as optimum conditions. The results are shown in figure 5.25.

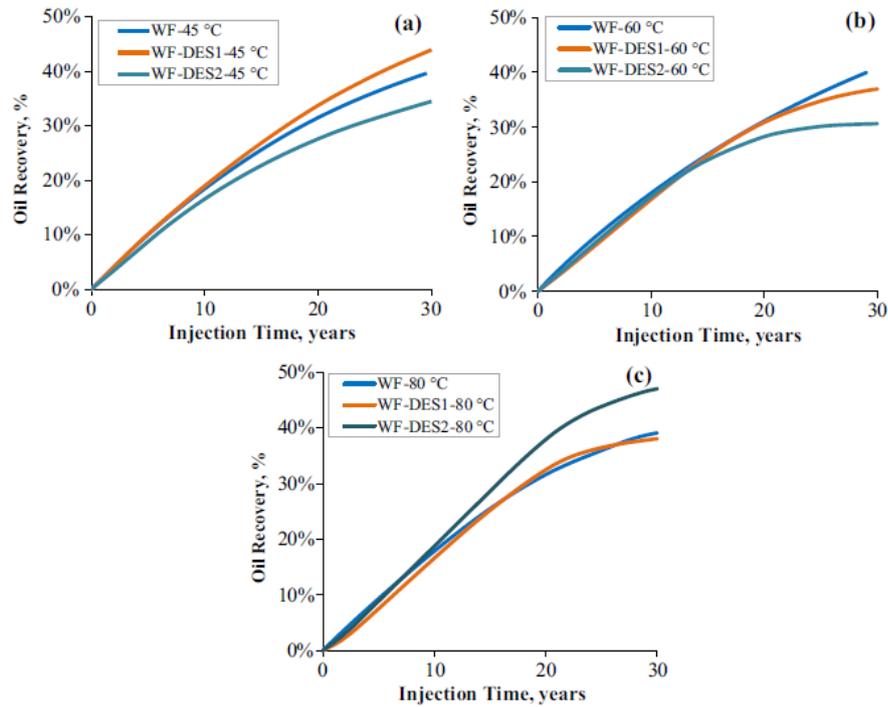


Fig. 5. 25: Oil Recovery by Waterflooding, Waterflooding (20 years)+DES1 (10 years) and Waterflooding (20 years)+DES2 (10 years) Injections (Source: Al-Rujaibi et al., 2016)

From figure 5.25 it can be detected that at 45 °C highest oil recovery was achieved with Water flooding+DES1 with a total oil recovery of 44 %OOIP. At 80 °C Water flooding+DES2 showed the highest oil recovery (47 %OOIP). This is in agreement with wettability alteration results which was analyzed based on relative permeability curves.

Sequential DESs (ChCl:Glycerol and ChCl:Urea) and Steam Injection

Mohsenzadeh et al. (2017) reported the results of core flooding tests in table 5.4 for different scenarios. Different concentrations of DESs are 100 vol% DES (undiluted DES), 50 vol% DES in brine (2-fold diluted DES), and 5 vol% DES in brine (20-fold diluted DES). We need to note that water flooding and DESs injections were carried out at 45°C, whereas steam injection was conducted at 260°C.

Tab. 5. 4: Oil Recovery Results From Core Flooding Tests (Source: Mohsenzadeh et al., 2017)

Test No.	1	2	3	4	5	6	7	8
Initially at 45 °C and 500 Psi, Then steam at 260 °C	Primary steam	Secondary steam after water flooding	Secondary steam after 1.5 PV undiluted DES1	Secondary steam after 1.5 PV undiluted DES2	Tertiary steam after 2F diluted DES1	Tertiary steam after 2F diluted DES2	Tertiary steam after 20F diluted DES1	Tertiary steam after 20F diluted DES2

Core Length, mm	97	97	99	97	97	97	98	92	
Core Diameter, mm	38	38	38	38	38	38	38	38	
Pore volume, cc	22.22	21.75	22.31	20.03	21.91	22.12	21.7	20.69	
Porosity, %	20.2	19.78	19.88	19.12	19.92	20.12	19.53	19.83	
Brine permeability, md	57	51.8	53.6	60.2	52.4	58.2	65.8	64.1	
IOIP, cc	17.4	17	17.0	16.7	17.1	16.8	17.4	16.6	
S _{oi} , %	78.3	77.5	76.2	83.3	78.0	75.9	80.2	80.2	
Recovery factor, % IOIP	Water flooding	-	30.6	-	-	34.5	32.7	34.5	36.1
	DES	-	-	45.8	50.3	11.7	14.6	6.9	7.8
	steam	55.9	43.5	34.1	35.9	29.2	35.1	29.3	30.1
	Total	55.9	74.1	79.9	86.2	75.4	82.4	70.7	74.0

Steam injection was performed for different modes as summarized below and total heavy oil recovery in %OOIP is reported in parentheses:

- Test 1: Steam injection alone (55.9%),
- Test 2: Water flooding+steam injection (74.1%),
- Test 3: 100 vol% DES1+steam injection (79.9%),
- Test 4: 100 vol% DES2+steam injection (86.2%),
- Test 5: 50 vol% DES1+steam injection (75.4%),
- Test 6: 50 vol% DES2+steam injection (82.4%),
- Test 7: Water flooding +5 vol% DES1+steam injection (70.7%)
- Test 8: Water flooding +5 vol% DES2+steam injection (74.0%).

As can be seen from table 5.4, the highest oil recovery was obtained from the injection of 100 vol% DES2 followed by steam injection (test 4). The effects of these studied DESs on increasing heavy oil recovery is due to wettability alteration and viscous forces. This was studied in the previous work of Mohsenzadeh et al. (2014) and explained in previous parts. In all cases, DES2 showed better performance than DES1 due to higher alkalinity and higher effect on wettability alteration. Moreover, Mohsenzadeh et al. (2017) presented the results of API measurement of oil which was conducted at 45 °C as shown in table 5.5.

Tab. 5. 5: API Gravity Modification and Desulfurization
(Source: Mohsenzadeh et al., 2017)

Test No.		1	2	3	4	5	6	7	8	
Initially at 45 °C and 500 Psi, Then steam at 260 °C	Original Oil	Primary steam	Secondary Steam after water flooding	Secondary steam after 1.5 PV undiluted DES1	Secondary steam after 1.5 PV undiluted DES2	Tertiary steam after 2F diluted DES1	Tertiary steam after 2F diluted DES2	Tertiary steam after 20F diluted DES1	Tertiary steam after 20F diluted DES2	
API of produced oil by steam flooding	°API	16.55	17.47	17.61	20.12	18.8	19.32	18.45	18.52	17.97
	°API change	0.0	+ 0.92	+ 1.06	+ 3.57	+ 1.25	+ 2.77	+ 1.9	+ 1.97	+ 1.42

Sulphur content of produced oil after steam flooding	Sulphur, wt %	2.680	2.660	2.667	2.234	2.444	2.331	2.505	2.648	2.650
	%, desulphurization	-	0.73	0.51	16.64	8.8	13.01	6.51	1.2	1.1

Original oil had 16.55 °API gravity. We can see from the table significant improvements of °API gravity which oil becomes lighter after steam injection. The highest increase was achieved with a 100 vol% DES1 injection followed by steam injection (test 3). In this case, API gravity increased from 16.55 to 20.12 (+3.57). Furthermore, table 16 summarizes the reduction of sulfur content of produced oil after tests. From the table, we can see a significant amount of sulfur reduction when DESs injected primarily (6.51%-16.64%) (Tests 3, 4, 5, 6). When water flooding performed before DESs injection or only steam injection alone, there is only a small amount of desulfurization (0.51%-1.2%) (Tests 1, 2, 7, 8). Test 3 (100 vol% DES1+steam injection) showed the highest desulfurization with 16.64% of sulfur reduction. In terms of desulfurization, DES1 showed better performance than DES2. This was explained as due to the higher availability of dissociable hydrogen in DES1 (OH⁻) compared to DES2 (NH₂⁻).

ChCl:Urea (DES1), ChCl:Thio urea (DES2), ChCl:Ethylene Glycol (DES3), ChCl:Glycerol (DES4)

El-hoshoudy et al. (2019) evaluated the oil recovery enhancement due to the DES solution by flooding tests. Initially, brine flooding performed followed by DES injection (50 vol %). The results are presented in figure 5.26.

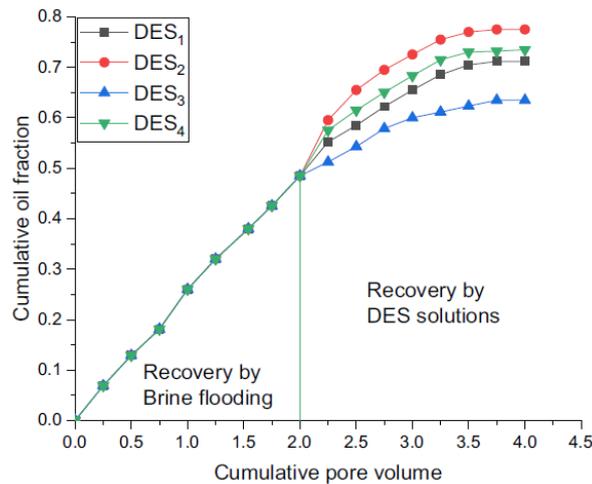


Fig. 5. 26: Oil Recovery Using Brine and DES Solutions (Source: El-hoshoudy et al., 2019)

Two pore volumes of brine flooding resulted in 48% of total oil recovery. After that, we can see an increase in oil recovery due to the injection of DES solutions (50 vol %). The highest recovery achieved with DES2 which recovery increases up to 77%. The authors explained the increase of oil recovery by DES solutions is due to the reduction of IFT and wettability alteration. Moreover, El-hoshoudy et al. (2019) conducted a simulation study to analyze the efficiency of DESs for improving oil recovery in the industrial scale. After brine flooding, DES solutions were injected. The results are shown in figure 5.27. DES2 showed the highest oil recovery value from the simulation study as well. This is in agreement with lab studies. The authors concluded that DESs are promising EOR agents.

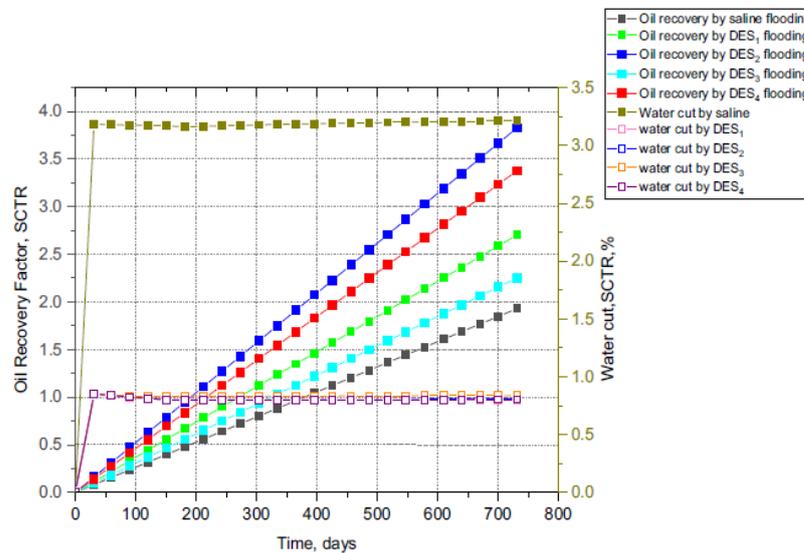


Fig. 5. 27: Oil Recovery and Water Cut for Brine and DES Solutions
(Source: El-hoshoudy et al., 2019)

Na₂CO₃:Glycerin (1:2) (DES3), Na₂CO₃:Urea (1:2) (DES4), C₁₀H₁₉N₃O₆:C₁₈H₃₀O₃S (1:10) (DES6), ChCl:C₁₈H₃₀O₃S (1:1) (DES7), Na₂CO₃:Na₂SO₄ (1:2) (DES9), Na₂CO₃:C₈H₁₅BF₄N₂ (5:1) (DES11), ChCl:Na₂CO₃ (1:2) (DES14)

Huang et al. (2020) conducted spontaneous imbibition tests to analyze the oil recovery from tight core samples using different chemicals, including DESs. Figure 5.28 shows results for different chemicals and DESs. It should be noted tests were performed using brine and deionized water (DI) for comparison purposes.

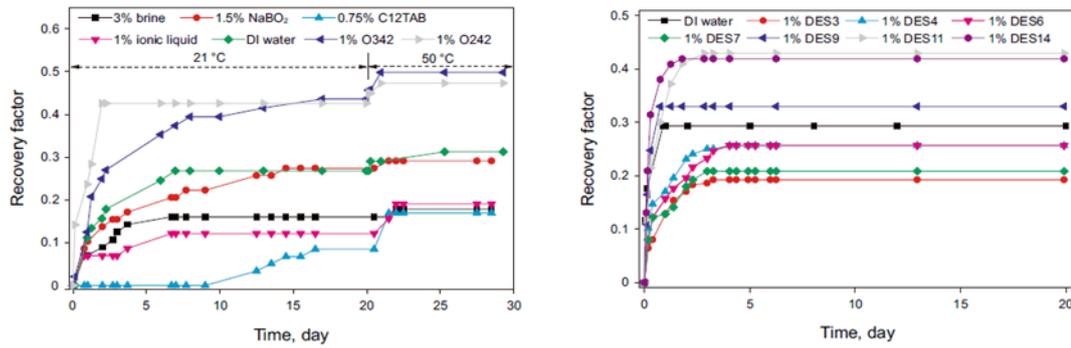


Fig. 5. 28: Oil Recovery from Tight Cores Using Different Chemicals (left) and DES Solutions (right) (Source: Huang et al., 2020)

Considering 10 days and 21 °C, the recovery factor from 1% ionic liquids is around 0.11 and this value is around 0.14 for brine. From figure 5.28 we can see all DESs showed higher recovery factors than ionic liquids and brine. DES11 and DES14 showed the highest recovery factor with around 42%. Interestingly, from IFT analysis we observed DES6 had better performance than DES14 in terms of IFT reduction. However, from figure 5.28 we see that DES14 showed a higher recovery factor (42%) than DES6 (25%). This indicates that IFT change might not be very important for oil recovery from tight sands. After studying change in wettability due to DESs, authors found out wettability alteration occurred and this plays the main role in oil recovery from tight sand cores.

5.5 Formation Damage

ChCl:Glycerol (DES1) and ChCl:Urea (DES2) (a)

After observing promising results from ChCl:glycerol and ChCl:urea on the EOR process, Mohsenzadeh, and co-workers studied the effects of ChCl:glycerol and ChCl:urea on formation damage. They performed core flooding tests at reservoir pressure (1200 psi) and at different temperatures to examine permeability change due to DES injection. Several factors including the water shock phenomenon were analyzed to understand the mechanism of formation damage. In water shock phenomenon formation damage occurs due to change in salinity that vanishes the equilibrium condition between rock and fluid. Mohsenzadeh et al. (2015b) investigated the effect of DESs injection for reducing water shock damage. The results are shown in figure 5.29.

Initially, the core sample was flooded with brine and followed by distilled water injection to see the water shock damage. This resulted in huge permeability reduction of 60%, 65% and 67% at 40°C, 60°C and 80°C, respectively. This is represented with a blue chart in figure 5.29. To see the effects of DESs injection on water shock damage reduction, after brine flooding DESs injections were performed and followed by distilled water injection. Results showed DESs were able to reduce water shock damage especially DES2 but due to precipitation and recrystallization processes, there was still some permeability reduction of core samples.

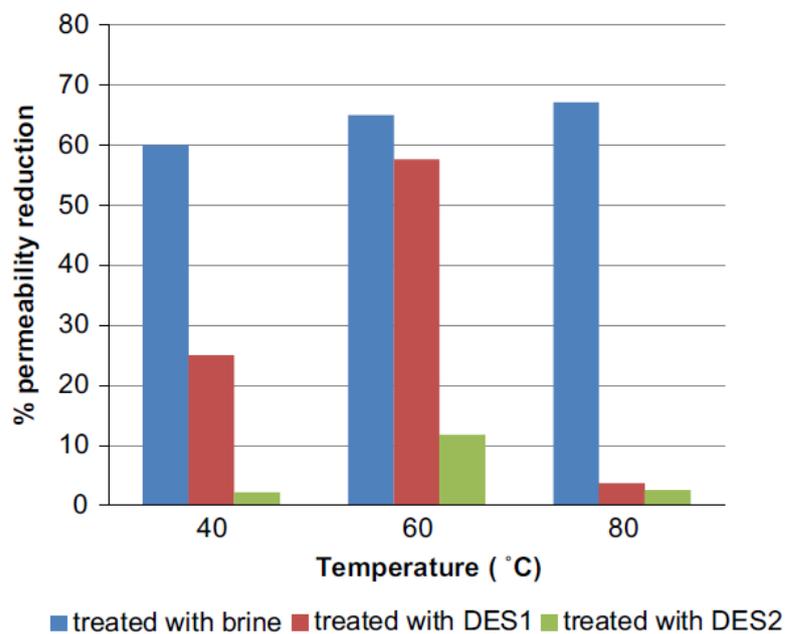


Fig. 5. 29: Effect of DESs on Reduction of Water Shock Damage
(Source: Mohsenzadeh et al., 2015b)

Choline Chloride (ChCl):Ethylene Glycol (EG) DES (a)

Shuwa et al. (2014) analyzed the formation damage due to DES injection by measuring absolute permeability before and after the DES injection. DES injection was allowed for 12 hours of aging. The results are shown in table 5.6.

Tab. 5. 6: Formation Damage Test Results for ChCl:EG (1:2)
(Source: Shuwa et al., 2014)

Experimental Conditions	Test number	1	2	3
	Temperature, °C	45	60	80
	Pressure, psi	1,200	1,200	1,200

Core Properties	Length, mm	68	76.2	73.2
	Diameter, mm	38.1	37.9	38.1
	Porosity, %	19.4	18.2	19.5
	Pore volume, cm ³	15.1	16.3	16.3
Absolute Permeability (md)	Before injection	48	49	45
	After aging	49	49	42
	Change, %	1	0	5

Test results didn't show any significant formation damage. There is only 1% of permeability reduction at 45°C, no permeability change at 60°C and 5% permeability reduction at 80°C. The authors explained the reason behind this is with increasing temperature, interactions between rock material and DES+brine solution increase as well causing the adsorption of a small amount of DES+brine solution due to mainly ion exchange and possible electrostatic forces as well. Rock material (Berea Sandstone) composed of 92% of quartz mineral which contains ions and these ions exchanges with the ions of DES+brine solution that results in the adsorption.

Choline Chloride (ChCl):Malonic Acid (MA) (1:1) and (2:1) (a)

Formation damage tests were performed by measuring absolute permeability and results showed there was not any significant permeability change occurred for both DESs at different temperatures (Al-Weheibi et al., 2015). The results are presented in table 5.7.

**Tab. 5. 7: Formation Damage Test Results for ChCl:MA (1:1) and (2:1)
(Source: Al-Weheibi et al., 2015)**

<i>System</i>	<i>Temperature °C</i>	<i>Perm. increments</i>
DES1	80	2.6%
	60	1.7%
	45	1.4%
DES2	80	1.9%
	60	1.6%
	45	1.2%

5.6 Analysis and Comparison between Performances of Tested DESs

Stable Emulsion Formation

Table 5.8 shows the list of DES solutions tested for emulsification. In all cases type of crude oil heavy oil.

Tab. 5. 8: Comparison of DESs on Emulsification

DES (Molar Ratio)	Stable Emulsion Formation	Reference
ChCl:Glycerol (1:2)	No	Mohsenzadeh et al. (2014)
ChCl:Urea (1:2)	No	Mohsenzadeh et al. (2014)
ChCl:EG (1:2)	No	Shuwa et al. (2014)
ChCl:MA (1:1)	Limited	Al-Weheibi et al. (2015)
ChCl:MA (2:1)	Limited	Al-Weheibi et al. (2015)

ChCl:Glycerol (1:2), ChCl:Urea (1:2), and ChCl:EG (1:2) didn't have the capacity to form an emulsion with heavy crude oil. Whereas, ChCl:MA (1:1) and ChCl:MA (2:1) DESs were able to form only a limited emulsion with heavy crude oil. The main reasons behind the non-achievement of stable emulsion formation are the immiscibility of DES solution with heavy crude oil and high IFT between DES solution and oil. IFT should be low enough for effective mixing but it was not a case for these studied DESs. IFT change for these and other studied DESs will be described more detailed in the below section.

IFT Change

One of the functions of surfactants is to reduce IFT between crude oil and brine solution and improve recovery. However, this behavior was observed only in some cases of DESs. Table 5.9 shows the effect of all studied DESs on IFT alteration.

Tab. 5. 9: Comparison of DESs based on IFT Change

DES (Molar Ratio)	Crude Oil Type	IFT Between Oil/Brine (mN/m)	IFT Between Oil/DES Solution (mN/m)	Reference
ChCl:Glycerol (1:2)	Heavy	6.4	36.7	Mohsenzadeh et al. (2014)
	Light	6.7	1.5	El-Hoshoudy et al. (2019)
ChCl:Glycerol (1:3)	Medium	23.2	0.2	Hadj-Kali et al. (2015)

ChCl:Urea (1:2)	Heavy	6.4	30.8	Mohsenzadeh et al. (2014)
	Light	6.7	4.3	El-Hoshoudy et al. (2019)
	Medium	23.2	0.2	Hadj-Kali et al. (2015)
ChCl:EG (1:2)	Heavy	6.4	11.4	Shuwa et al. (2014)
	Light	6.7	5	El-Hoshoudy et al. (2019)
ChCl:MA (1:1)	Heavy	6.4	21.9	Al-Weheibi et al. (2015)
ChCl:MA (2:1)	Heavy	6.4	21.9	Al-Weheibi et al. (2015)
ChCl:Thio Urea (1:2)	Light	6.7	0.6	El-Hoshoudy et al. (2019)
$C_{10}H_{19}N_3O_6$ ⁽¹⁾ : $C_{18}H_{30}O_3S$ ⁽²⁾ (1:10)	Light	25	1.5	Huang et al. (2020)
ChCl:Na ₂ CO ₃ (1:2)	Light	25	7	Huang et al. (2020)

⁽¹⁾ *N, N*-bis (2-[bis(carboxymethyl)amino]ethyl) glycine

⁽²⁾ Dodecylbenzenesulfonic acid

For heavy crude oils, the injection of DES solutions increased IFT rather than decrease as shown in table 5.9 and figure 5.30. This is believed due to weaker interaction between functional groups of DES and oil due to van der Waals force which results in higher IFT compared to brine/oil IFT. Besides, there might be significant coulombic attraction forces because of the presence of larger cations such as choline ions in DESs. Furthermore, IFT values decreased with the increase in temperature regardless of crude oil type.

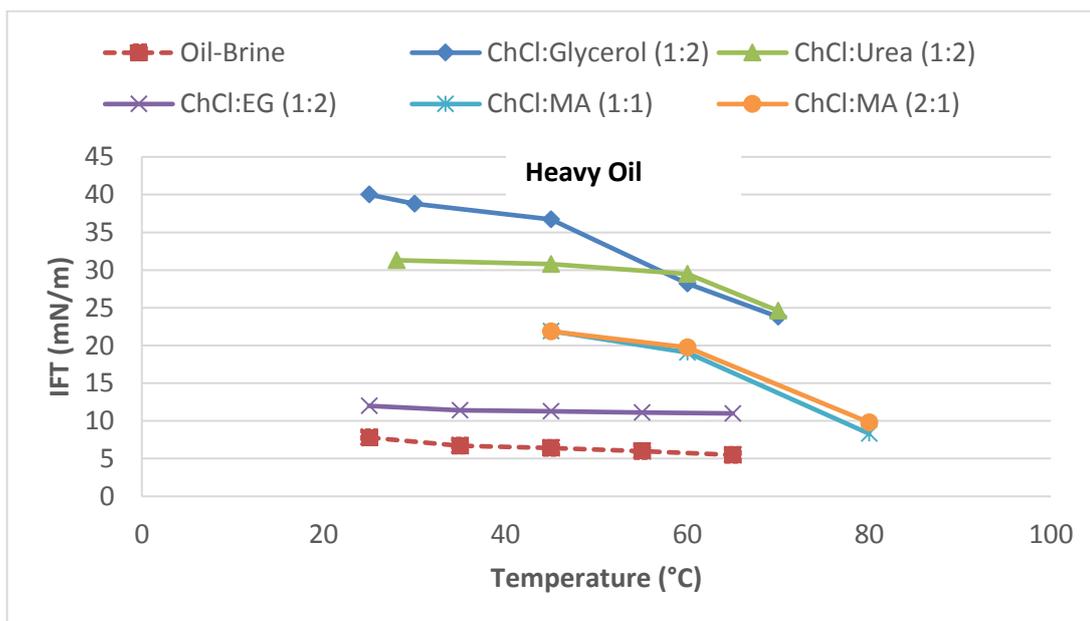


Fig. 5. 30: IFT Values between Heavy Oil/Brine and Heavy Oil/DESs at Different Temperatures

On the other hand, the introduction of DESs showed a decrease in IFT values between oil/DES solution for light and medium crude oils. These are shown in figure 5.31, 5.32 for light oil reservoirs, and in figure 5.33 for medium oil reservoirs.

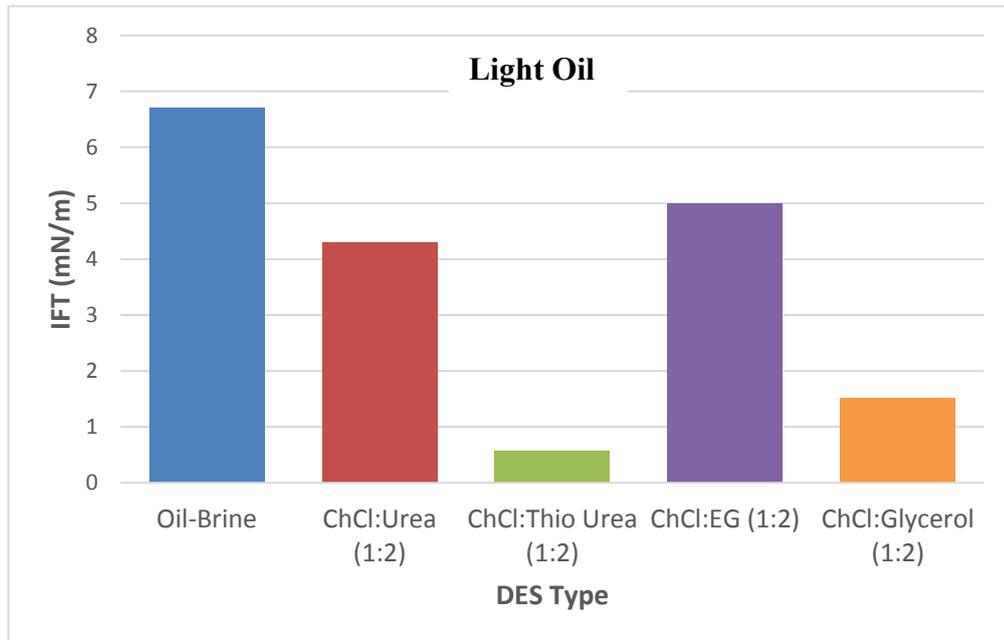


Fig. 5. 31: IFT Values between Light Oil/Brine and Light Oil/DESs at 40°C

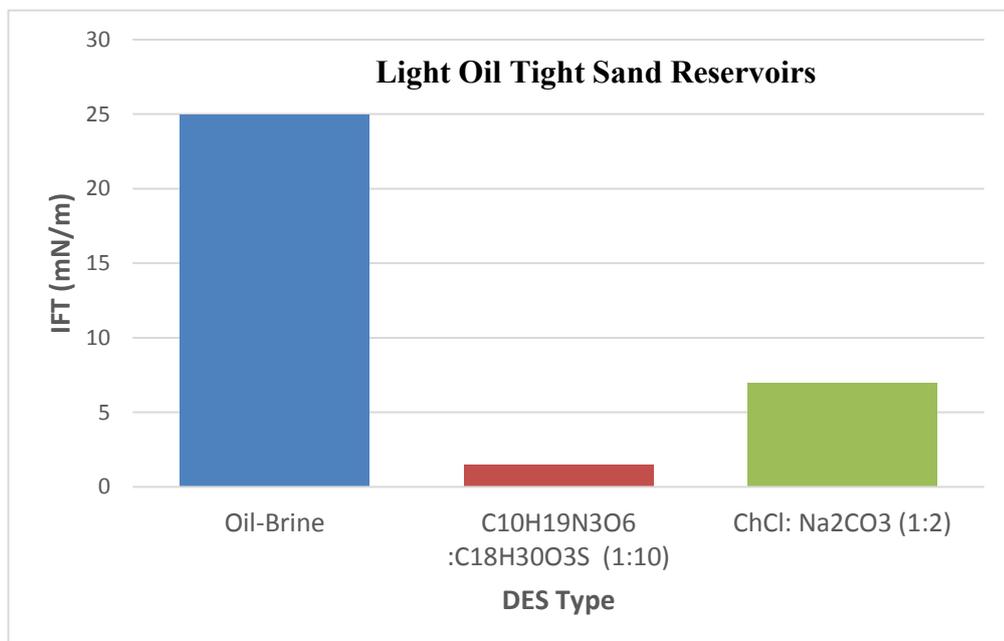


Fig. 5. 32: IFT Values between Light Oil/Brine and Light Oil/DESs at 25°C

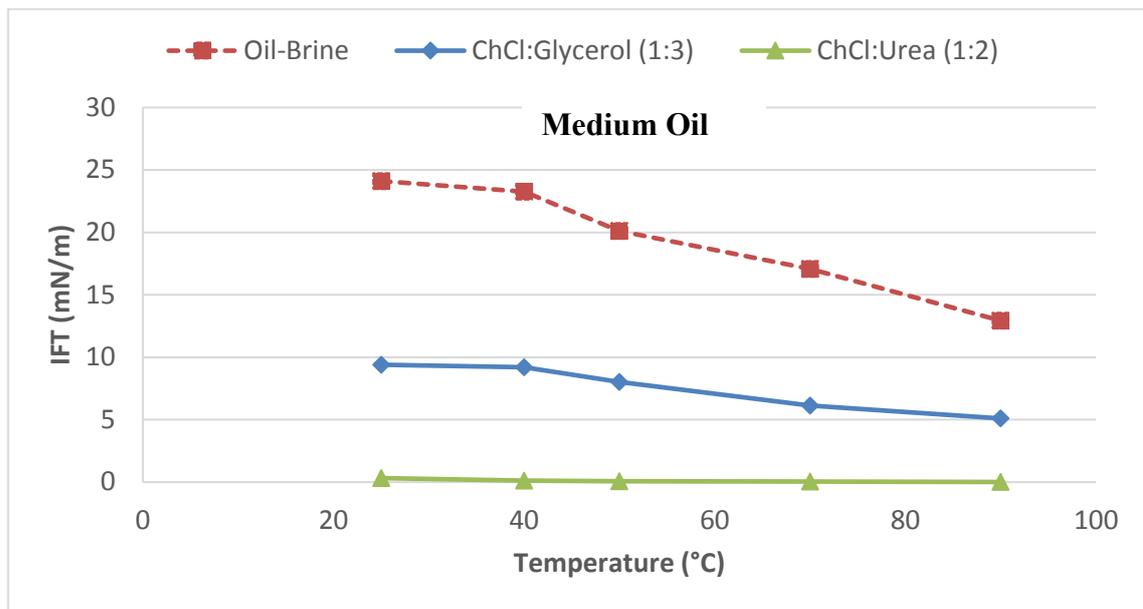


Fig. 5. 33: IFT Values between Medium Oil/Brine and Medium Oil/DESs

Wettability Alteration

Wettability alteration is another important mechanism for the enhancement of oil recovery. All studied DESs were able to alter wettability towards the less oil-wet condition. This leashes more oil from the rock surface and increases oil recovery. Names of studied DESs are shown in table 5.10.

Tab. 5. 10: List of Tested DESs for Wettability Alteration

DES (Molar Ratio)	Wettability Change	Reference
ChCl:Glycerol (1:2)	Yes	Mohsenzadeh et al. (2014)
	Yes	El-Hoshoudy et al. (2019)
ChCl:Urea (1:2)	Yes	Mohsenzadeh et al. (2014)
	Yes	El-Hoshoudy et al. (2019)
ChCl:EG (1:2)	Yes	Shuwa et al. (2014)
	Yes	El-Hoshoudy et al. (2019)
ChCl:MA (1:1)	Yes	Al-Weheibi et al. (2015)
	Yes	Al-Rujaibi et al. (2016)

ChCl:MA (2:1)	Yes	Al-Weheibi et al. (2015)
	Yes	Al-Rujaibi et al. (2016)
ChCl:Thio Urea (1:2)	Yes	El-Hoshoudy et al. (2019)
Na ₂ CO ₃ :Glycerin (1:2)	Yes	Huang et al. (2020)
Na ₂ CO ₃ :Urea (1:2)	Yes	Huang et al. (2020)
ChCl:Na ₂ CO ₃ (1:1)	Yes	Huang et al. (2020)
C ₁₀ H ₁₉ N ₃ O ₆ :C ₁₈ H ₃₀ O ₃ S (1:10)	Yes	Huang et al. (2020)
ChCl:C ₁₈ H ₃₀ O ₃ S (1:1)	Yes	Huang et al. (2020)
Na ₂ CO ₃ :Na ₂ SO ₄ (1:2)	Yes	Huang et al. (2020)
Na ₂ CO ₃ :C ₈ H ₁₅ BF ₄ N ₂ (5:1)	Yes	Huang et al. (2020)
ChCl:Na ₂ CO ₃ (1:2)	Yes	Huang et al. (2020)

Formation Damage

To analyze the formation damage effect of DESs, permeability was measured before and after the DES injection and there was not significant permeability change as it can be seen from table 5.11. In the worst case, maximum permeability reduction was %5 from ChCl:EG (1:2). ChCl:MA DESs resulted in an insignificant increase of permeability. ChCl:Glycerol (1:2) and ChCl:Urea (1:2) showed a positive impact on the reduction of water shock damage.

Tab. 5. 11: Formation Damage Effects of Studied DESs

DES (Molar Ratio)	Permeability Change	Reference
ChCl:Glycerol (1:2)	Reduced Water Shock Damage	Mohsenzadeh et al. (2015)
ChCl:Urea (1:2)	Reduced Water Shock Damage	Mohsenzadeh et al. (2015)
ChCl:EG (1:2)	Reduced (1-5 %)	Shuwa et al. (2014)
ChCl:MA (1:1)	Increased (1-3 %)	Al-Weheibi et al. (2015)
ChCl:MA (2:1)	Increased (1-2 %)	Al-Weheibi et al. (2015)

Oil Recovery Improvement

The effects of tested DESs on different mechanisms of EOR processes are summarized in table 5.12. As can be seen from the table, DESs are able to increase oil recovery as an EOR agent. Wettability alteration was the main mechanism for the improvement of oil recovery. Total oil recovery and additional oil recovery due to DESs injection after brine flooding are reported in the table at different temperatures. With increasing temperature, oil recovery values also increased. The range of additional oil recovery by DES injection is between 4-30 %OOIP. This summary table is presented to show experimental conditions, core sample properties and crude oil types are not the same in all cases.

Tab. 5. 12: Comparison of Performance of Tested DESs in EOR Processes

DESs	Properties of Core Sample / Average Porosity and Permeability	Crude Oil Type	Stable Emulsion Formation	IFT Between Oil/DES Solution	Wettability Alteration	Total Recovery at 45°C-80°C (%OOIP)	Additional Recovery due to DES Injection After Brine Flooding at 45°C-80°C (%OOIP)	Reference
ChCl:Glycerol (1:2)	$\Theta=18-20\%$ $k=12-32$ mD	Heavy	No	Increase	Yes	50%-71%	14%-30%	Mohsenzadeh et al. (2014)
	Sand Pack	Light	–	Decrease	Yes	73% (at 93°C)	25% (at 93°C)	El-hoshoudy et al (2019)
ChCl:Glycerol (1:2) + Steam ⁽¹⁾	$\Theta=18-20\%$ $k=12-32$ mD	Heavy	–	–	–	75% (at 45°C)	12% (at 45°C)	Mohsenzadeh et al. (2017)
ChCl:Glycerol (1:3)	–	Medium	–	Decrease	–	–	–	Hadj-Kali et al. (2015)
ChCl:Urea (1:2)	$\Theta=18-20\%$ $k=12-32$ mD	Heavy	No	Increase	Yes	60%-71%	23%-26%	Mohsenzadeh et al. (2014)
	Sand Pack	Light	–	Decrease	Yes	70% (at 93°C)	22% (at 93°C)	El-hoshoudy et al. (2019)
	–	Medium	–	Decrease	–	–	–	Hadj-Kali et al. (2015)
ChCl:Urea (1:2) + Steam ⁽¹⁾	$\Theta=18-20\%$ $k=12-32$ mD	Heavy	–	–	–	82% (at 45°C)	15% (at 45°C)	Mohsenzadeh et al. (2017)
ChCl:EG (1:2)	$\Theta=17-20\%$ $k=13-62$ mD	Heavy	No	Increase	Yes	25%-85%	6%-16%	Shuwa et al. (2014)

	Sand Pack	Light	–	Decrease	Yes	62% (at 93°C)	14% (at 93°C)	El-hoshoudy et al. (2019)
ChCl:MA (1:1)	$\Theta=21\%$ and $k=230$ mD	Heavy	Limited	Increase	Yes	41%-52%	6%-8%	Al-Weheibi et al. (2015)
	$\Theta=21\%$ and $k=205$ mD	Heavy	–	–	Yes	44% (at 45°C)	10% (at 45°C)	Al-Rujaibi et al. (2016)
ChCl:MA (2:1)	$\Theta=21\%$ and $k=230$ mD	Heavy	Limited	Increase	Yes	48%-54%	4%-8%	Al-Weheibi et al. (2015)
	$\Theta=21\%$ and $k=205$ mD	Heavy	–	–	Yes	36% -47%	8%-10%	Al-Rujaibi et al. (2016)
ChCl:Thio Urea (1:2)	Sand Pack	Light	–	Decrease	Yes	77% (at 93°C)	29% (at 93°C)	El-hoshoudy et al. (2019)
Na ₂ CO ₃ : Glycerin (1:2)	$\Theta=7\%$ and $k=0.1$ mD	Light	–	–	Yes	19% (at 50°C)	–	Huang et al. (2020)
Na ₂ CO ₃ :Urea (1:2)	$\Theta=7\%$ and $k=0.1$ mD	Light	–	–	Yes	25% (at 50°C)	–	Huang et al. (2020)
ChCl: Na ₂ CO ₃ (1:1)	$\Theta=7\%$ and $k=0.1$ mD	Light	–	–	Yes	–	–	Huang et al. (2020)
C ₁₀ H ₁₉ N ₃ O ₆ ⁽²⁾ : C ₁₈ H ₃₀ O ₃ S ⁽³⁾ (1:10)	$\Theta=7\%$ and $k=0.1$ mD	Light	–	Decrease	Yes	25% (at 50°C)	–	Huang et al. (2020)
ChCl: C ₁₈ H ₃₀ O ₃ S ⁽³⁾ (1:1)	$\Theta=7\%$ and $k=0.1$ mD	Light	–	–	Yes	21% (at 50°C)	–	Huang et al. (2020)
Na ₂ CO ₃ : Na ₂ SO ₄ (1:2)	$\Theta=7\%$ and $k=0.1$ mD	Light	–	–	Yes	33% (at 50°C)	–	Huang et al. (2020)
Na ₂ CO ₃ : C ₈ H ₁₅ BF ₄ N ₂ ⁽⁴⁾ (5:1)	$\Theta=7\%$ and $k=0.1$ mD	Light	–	–	Yes	43% (at 50°C)	–	Huang et al. (2020)
ChCl: Na ₂ CO ₃ (1:2)	$\Theta=7\%$ and $k=0.1$ mD	Light	–	Decrease	Yes	42% (at 50°C)	–	Huang et al. (2020)

(1) Steam injection performed at 260°C

(2) *N, N*-bis (2-[bis(carboxymethyl)amino]ethyl) glycine

(3) Dodecylbenzenesulfonic acid

(4) 1-butyl-3-methylimidazolium tetrafluoroborate

In order to compare them at similar conditions, they were divided into three groups based on experimental conditions, core properties, and oil type. DESs were compared according to additional oil recovery within each corresponding belonging group.

Group 1: Experimental temperature is 80°C. Oil type is heavy oil. Core properties are 17-20% of porosity and 12-62 mD of permeability.

Group 2: Temperature is 93°C. Oil type is light oil. The sand packed model was used for core flooding tests to represent a coarse reservoir.

Group 3: Temperature is 80°C. Oil type is heavy oil. Core properties are 21% of average porosity and 230 mD of average permeability.

The results are shown in figure 5.34. At the conditions of group 1, ChCl:Glycerol (1:2) showed the best performance with an additional oil recovery of 30 %OOIP. Under the conditions of group 2, the best performance was achieved with ChCl:Thio Urea (1:2) with 29 %OOIP. Both molar ratios of ChCl:Malonic Acid (1:1) and (1:2) showed 8 %OOIP.

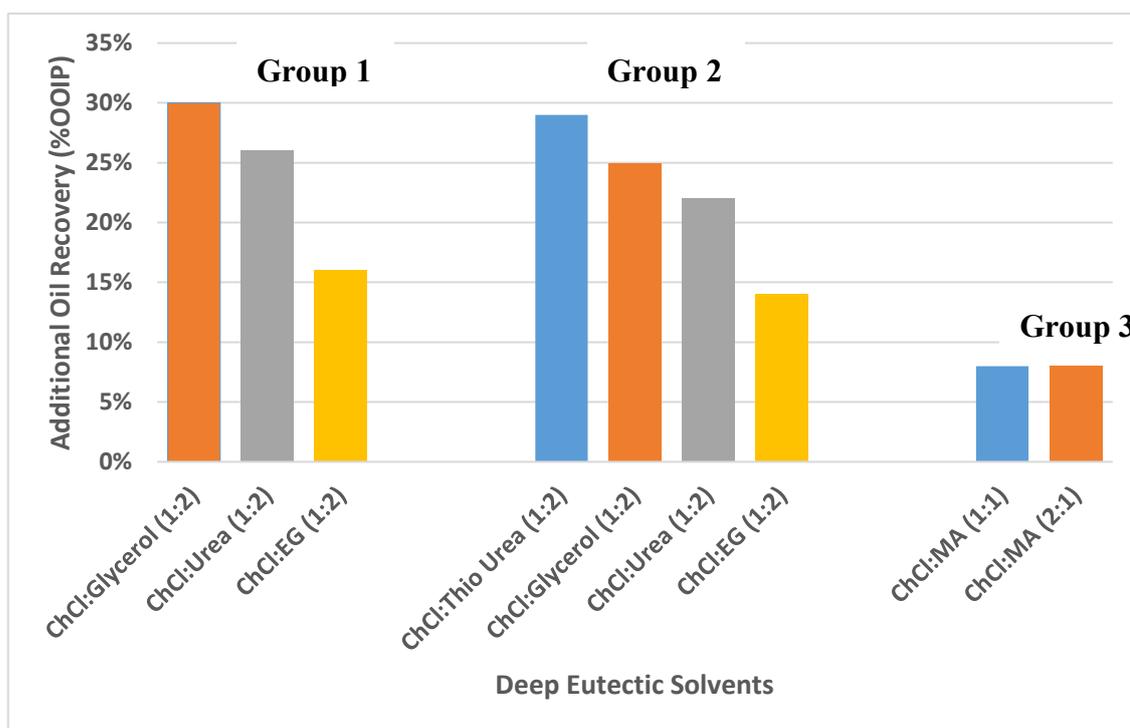


Fig. 5. 34: Comparison of Tested DESs According to Similar Conditions

Additional oil recovery from tight sands was not considered in this graph because they were not performed after brine flooding. They were injected initially as a first stage to displace oil without brine flooding. So they were compared with each other based on total oil recovery and results are shown in figure 5.35. The best performance was

achieved with Sodium Carbonate (Na_2CO_3) and 1-butyl-3-methylimidazolium tetrafluoroborate ($\text{C}_8\text{H}_{15}\text{BF}_4\text{N}_2$) (5:1) with a total recovery of 43 %OOIP.

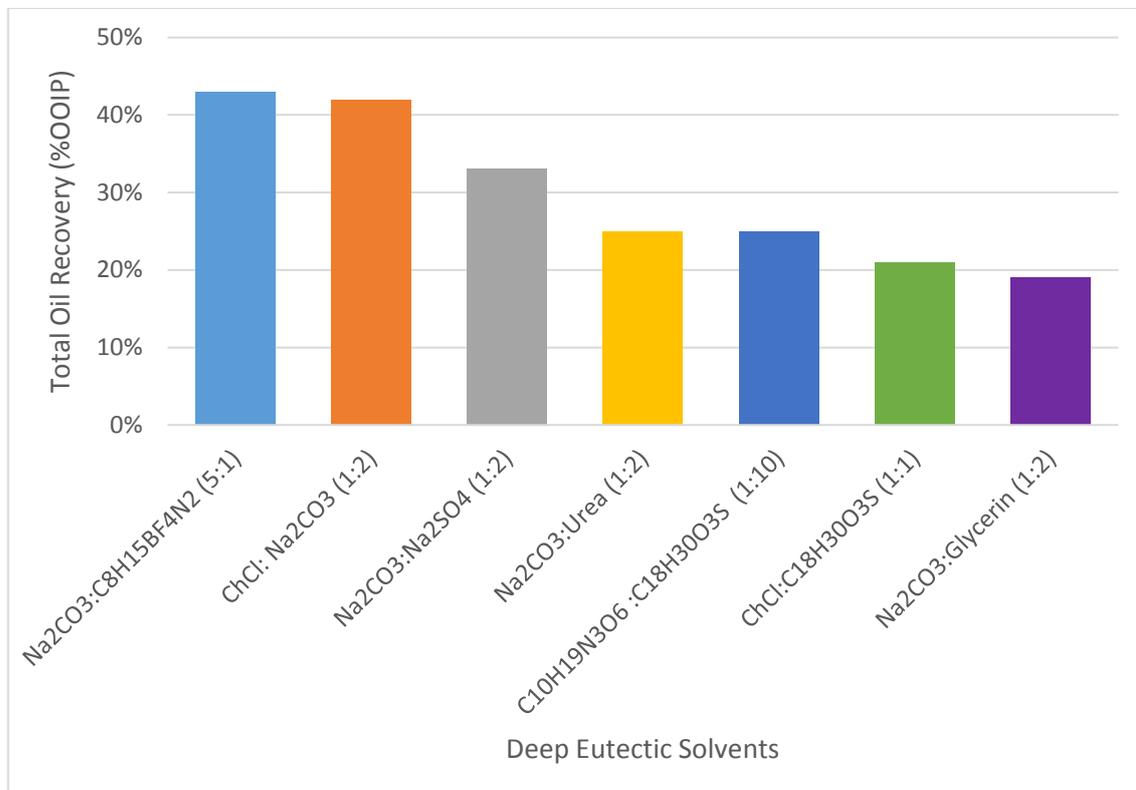


Fig. 5. 35: Comparison of DESs According to Total Oil Recovery from Tight Sands via Spontaneous Imbibition Tests

5.7 Economic Aspect

Cost of an EOR technology is one of the important parameters as screening criteria for projects. According to my knowledge, there are no studies about the economic evaluation of DESs in EOR. So it is essential to look at some economic parameters in order to give an idea for future works. As a DES, the price of $\text{ChCl}:\text{Urea}$ (1:2) will be considered. Its price is only 10% of the typical ILs (Su, 2009, Ma et al., 2017). The common price of ILs is around 6 \$/kg (Ma et al., 2018). Hence, the estimated price of $\text{ChCl}:\text{Urea}$ (1:2) will be around 0.6 \$/kg.

The cost of $\text{ChCl}:\text{Urea}$ (1:2) per one cubic meter of the injected solution was calculated based on the following equation:

$$\text{Cost}/\text{m}^3 = C * \text{Cost}/\text{g} \quad (5.1)$$

Where:

$\text{Cost}/\text{m}^3 = \text{Cost of ChCl:Urea per m}^3 \text{ of injected solution } (\$/\text{m}^3)$

$C = \text{Concentration of DES } (\text{g}/\text{m}^3)$

$\text{Cost}/\text{g} = \text{Cost of ChCl:Urea per g } (\$/\text{g})$

The concentration of DES used is $3000 \text{ g}/\text{m}^3$. This concentration was observed and proposed as an optimum value by Hadj-Kali et al. (2015) for applications of DESs in EOR. Therefore, the calculated cost of DES is $\$1.8$ per m^3 of the injected solution. 0.1-0.3 PV of a solution is injected in alkaline-surfactant-polymer flooding (Ghadami et al., 2015, Al-Murayri et al., 2018). The volume of the injected DES solution is taken as 0.2 PV.

For pore volume, Sabriyah Lower Burgan (SALB) reservoir considered. This reservoir is located in the north of Kuwait city. Reservoir parameters are available in the literature and reported in table 5.13.

Tab. 5. 13: Reservoir Parameters of Sabriyah Lower Burgan (Al-Murayri et al., 2018)

SALB Reservoir and Fluid Characteristics	
Lithology	sandstone
Percent Clay	4
Depth (ft)	8100
Porosity (fraction)	0.206 - 0.236
Average Permeability (mD)	550
Net Thickness (ft)	62.5
Temperature (°C)	82
Reservoir Pressure (psi)	3200
Crude Oil API Gravity (deg)	33
Crude Oil Viscosity at 83°C cP	0.79

The application of various EOR methods was evaluated for this reservoir before. Those methods are injection of CO_2 , N_2 , low salinity flooding, polymer, surfactant-polymer, alkaline-surfactant-polymer, and thermal methods (Al-Murayri et al., 2017, 2018, Al-Ghnemi et al., 2019).

The pore volume of this reservoir is $16.7 \times 10^6 \text{ m}^3$. As a result, $3.34 \times 10^6 \text{ m}^3$ solution will be injected. The total cost of DES will be \$6,012,000. This value is without considering the recyclability of DESs. Recyclability is one of the characteristics of DESs and when this is taken into account the total cost of the required DES will be much lower.

For capital expenditures, facility and new wells costs are the main parameters. ASP plant with 10,000 bbl/day injection rate cost is approximately \$8.5 million and the cost of SP or polymer plants are around a third to half of ASP plant's cost (Al-Murayri et al., 2018). It is believed DES plant cost will be lower than these costs due to fewer components requirement but detailed analysis needs to be performed. For this reservoir, new production well costs \$4 million and \$3 million for injection wells (Al-Ghnemi, 2018). If previously drilled wells can be used for injection, costs will be reduced.

“For chemical floods where incremental costs are calculated, operating costs are minimal and are mainly borne by oil production from the conventional production technique” (Al-Murayri et al., 2018). Additional operating costs due to chemical injection such as transportation, injection, maintenance, lifting, labor, and utilities should be considered if the conventional production technology is at the end of its life (Al-Murayri et al., 2018). Al-Ghnemi (2018) presented some of those operating costs as shown in table 5.14.

**Tab. 5. 14: Categories of Operational Expenditures
(Al-Ghnemi, 2018)**

OPEX	Costs
Lifting Cost	0.85 \$/bbl
Water Handling Costs	0.05 \$/bbl
Water Injection Costs	0.1 \$/bbl
Fixed Costs (Annual)	60,000 \$
Water Softening Costs	0.5 \$/bbl

6 CONCLUSION & RECOMMENDATIONS

6.1 Conclusion

DESs were evaluated as a novel EOR method. Different aspects of DESs and their effects on different EOR mechanisms were analyzed. The performances of DESs were compared with each other. The following conclusions can be made:

- Tested DESs in EOR processes were able to increase oil recovery.
- Temperature has a positive impact on oil recovery enhancement which recovery increases with increasing temperature.
- Wettability alteration was a dominant mechanism for oil recovery improvement.
- The majority of tested DESs didn't show any stable emulsion formation with oil. Only malonic acid-based DESs had a limited capacity to form an emulsion.
- DESs resulted in IFT reduction in light and medium oil reservoirs. However, for heavy oil reservoirs, DESs caused an increase of IFT rather than a decrease.
- DESs didn't show any formation damage effect.
- Considering additional oil recovery due to DES injection after brine flooding, the best performance was seen in ChCl:Glycerol (1:2) with an additional oil recovery of 30 %OOIP.
- Total oil recovery values increased even higher values when steam flooding performed after the DES injection.
- Economic aspect was also analyzed which showed the cost of ChCl:Urea (1:2) DES is around \$1.8/m³ of injected DES/Brine solution without capital expenditures.
- DESs showed promising results as a novel EOR method. But only a few experimental and simulation studies were conducted until nowadays. Hence, it is still at the early stage of development.

6.2 Recommendations

Some recommendations can be proposed for future works and developments:

- Almost all of the previous studies were done based on ChCl -based DESs. More studies can be performed using a different type of DESs for comparison purposes.
- Previous studies were conducted using sandstone core samples. Different studies should be done for other types of core samples such as limestone.
- Field tests are recommended to analyze the industrial application.
- Until now there were no studies conducted about the economic evaluation of DESs in EOR. Therefore a detailed techno-economic analysis is necessary.

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