Performance Evaluation of Tetrabutylammonium Bromide-Based Deep Eutectic Solvents in Enhanced Oil Recovery of Nigerian Heavy Oil

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PERFORMANCE EVALUATION OF TETRABUTYLAMMONIUM BROMIDE-BASED DEEP EUTECTIC SOLVENTS IN ENHANCED OIL RECOVERY OF NIGERIAN HEAVY OIL

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ABSTRACT
Deep eutectic solvent (DES) is used as a green solvent in science due to its benefits over ionic liquids, such as biocompatibility and biodegradability, chemical stability with water, ease of preparation, and non-toxicity.DES 1 was successfully synthesized in a 1:2 molar ratio of Tetrabutylammonium bromide (TBAB) and polyethylene glycol 400 (PEG 400), while the novel DES 2 and DES 3 were synthesized in a 1:6 molar ratio of TBAB/ dimethyl sulfoxide (DMSO), and TBAB/N,N-dimethyl formamide (DMF) respectively. The performance(s) of the three DESs in the enhancement of heavy Nigerian crude oil recovery at ambient temperature was investigated. DES 1 recovered additional 16.07 % oil from core flooding using Berea sandstone core sample, resulting in an overall recovery of 53.44 %. DES 1 also resulted in an incremental recovery of 35.94 % from Niger-Delta sandstone, with a high ultimate recovery of 85.94 %. The presence of DES 2 and DES 3 were also shown to result in additional oil recovery. A drastic IFT reduction from 5.19 to 2.46mN/m was observed between the oil and the DES2 phase. Thus the study confirms that the presence of TBAB-based DES promotes reduction in the viscosity of the heavy oil and results in more oil recovery.

Keywords: *Deep eutectic solvents (DES), enhanced oil recovery, interfacial tension, tetrabutylammoniumbromide (TBAB)*

1. INTRODUCTION

As environmental awareness increases around the world, there has been a surge of interest in green solvents to supplement or substitute the existing non-green chemicals(Merchan-Arenas &Villabona-Delgado, 2019).Rapid biodegradability, low toxicity, non-flammability, low volatility, widespread availability and recyclability are the main characteristics of green solvents (Tarczykowska, 2017). Examples of green solvents used in oil recovery are water, supercritical fluids, non-toxic liquid polymers and their varied combinations, alkalis, biopolymers and bio-surfactants (Tackie-Otoo et al., 2020), nanoparticles (Orodu et al., 2019; Zargar et al., 2020), switchable hydrophilic solvent (SHS) like tertiary amines (Wang et al., 2019) and ionic liquids (Manshad et al., 2017). Poor biodegradability, high cost of synthesis and significant toxicology (El-hoshoudy et al., 2019) are the set back of ionic liquids (ILs), which has led to interest in another class of Ionic Liquid (IL-analogue) called Deep Eutectic Solvent (DES).

DES is a liquid that is usually made up of two or more elements that can self-associate, often by hydrogen bond interactions, to form an eutectic mixture with a melting point lower than the melting point of each individual component (Mohsenzadeh et al., 2015). It is used as a green solvent in science and industry due to its benefits over ionic liquids, such as biocompatibility and biodegradability, chemical stability with water, ease of preparation, and non-toxicity. They are often applied in the oil sector, specifically in EOR applications because of their polarity, high viscosity, and high thermal stability (El-hoshoudy et al., 2019; Mohsenzadeh et al., 2017). DESs have only recently gained interest, so studies on their use in the oil sector are limited. It was used as a novel chemical for heavy oil recovery by Mohsenzadeh et al. (2015), and later modified by dissolving Molybdenum oxide catalyst in DES (Choline Chloride/Urea) in the catalytic upgrading reaction of heavy crude oil. Mohsenzadeh et al. (2017), proposed and experimentally investigated concurrent DES and steam flooding as a new setting for heavy oil recovery enhancement, with potential for in-situ heavy oil upgrade using interfacial tension (IFT) and contact angle monitoring. The DESs were reported to be prominent and promising in altering rock wettability, decreasing the IFT between oil and water, lowering capillary pressure, and increasing injected solution viscosity, thereby improving heavy oil recovery and upgrading. Hadj-Kali et al. (2015) used separate amounts of the DESs (ChCl/glycerol and ChCl/urea) and their individual constituents as surfactants to reduce the IFT between crude oil and brine at ambient pressure and temperatures. It was determined that when the water content is less than 25 vol%, the interactions of the DES components become small, and the addition of 50 vol% water breaks the hydrogen bonding, resulting in no interactions between the hydrogen bond donor (HBD) and the salt. Hanamertani et al. (2017) used the Langmuir-Freundlich isotherm model to reduce surfactant adsorption on Berea sandstone during chemically enhanced oil recovery by using an imidazolium-based ionic liquid and a deep eutectic solvent as adsorbate material. Choline chloride-based DES with urea, thiourea, ethylene glycol and glycerol were experimentally and theoretically carried out by El-hoshoudy et al. (2019). An oil recovery of 77.4% was obtained at the laboratory scale, which is similar to that of a field scale, using Computer Modelling Group (CMG) software on a three- dimensional reservoir model. Sanati et al. (2021) compared an acidic DES (choline chloride:citric acid (1:1)) and an IL (1-dodecyl-3-methylimidazolium chloride) as chemical agents for enhanced oil recovery via experimental and theoretical investigations. The work showed that the core flooding of IL and DES-cetyltrimethylammoniumbromide (CTAB) mixtures obtained63.1% and 54.7 % recovery of the initial oil in place, respectively, and the adsorption of IL and DES was significantly lower than CTAB, with DES showing the least adsorption on dolomite surface.

Choline chloride-based-DES is the most widely used DES for EOR, as evident by some of the works mentioned above. However, choline-based-DESs are highly viscous solvents and are less effective in forming aqueous biphasic systems (Ijardar, 2020) required for the IFT reduction of heavy oil–water interface. High DES concentration or use of co-surfactant at low DES concentration have also been the demerits of the aforementioned DESs and these reduce the economic feasibility of employing DES at the industrial level. Thus, a rigorous analysis is needed to assess the efficiency of new tertiary ammonium salts. One of such salts is Tetrabutylammonium bromide (TBAB). TBAB is a quaternary ammonium salt, which may be explored as a potential substitute to other salts like chloline chloride. It is recyclable, simple to operate, non-corrosive, environmentally friendly with greater selectivity, and often known as a phase-transfer catalyst in different organic modifications (Yusof et al., 2014).

This research is focused on the synthesis of different DES, using tetrabutylammonium bromide (TBAB) as salt and polyethylene glycol (PEG) 400, dimethyl sulfoxide (DMSO), and N,N-dimethyl formamide (DMF as hydrogen bond donors (HBD), and the investigation of their performance(s) on enhanced oil recovery and IFT reduction, using Niger-Delta and Berea core samples.

2.0MATERIALS AND METHODS

2.1 Materials

A Nigerian heavy crude oil sample was obtained and characterized. Tetrabutylammonium bromide was purchased from Shangai Mackline Biochemical Co. Ltd., Shangai China, Polyethylene glycol 400 from BHD Laboratory Supplies Pooles, BH 15 1 TD, England, Dimethyl sulfoxide from Merck KGaA 64271 Darmstadt, Germany, and N,N-dimethyl formamide from Riedel-de Haen Ag Seelze-Hannover, Germany. All the chemicals had 98% purity and were used in the synthesis of DESs without any prior purification or drying.

2.2 Preparation of the DESs

DESs samples were synthesized as reported in literature(Ijardar, 2020).Tetrabutylammonium bromide (TBAB) was used as salts, while polyethylene glycol 400 (PEG 400), dimethyl sulfoxide (DMSO) and N,N-dimethyl formamide (DMF) as hydrogen bond donors (HBD), in the molar ratio of1:2 for DES 1, and ratio of 1:6 for DES 2 and DES 3, following a preliminary study, which showed that a molar ratio of 1:2 was not feasible for the synthesis of the novel DES 2 and DES 3. To combine the salt and the hydrogen bond donor, a magnetic stirrer (Stuart, Scientific Model US152) was used. Each DES mixture was stirred for 1 hour at 1000 rpm and 80 °C before a homogeneous transparent colorless liquid was obtained. DES samples were synthesized at atmospheric pressure.TBAB/PEG 400 was named DES 1, TBAB/DMSO as DES 2, and TBAB/DMF as DES 3.

2.3 Determination of physical properties of oil and core samples

Kinematic viscosity and specific gravity of the crude oil were determined at 27^{o}C using a digital viscometer (modelNTV-E1) and Attension tensiometer (Sigma 703D) respectively. API gravity was calculated from the specific gravity obtained. While the length and diameter of core samples (made from Berea and Niger-Delta sandstone) were measured with a vernier caliper.

2.4 Core flooding test

The experiment was carried out at the Department of Petroleum Engineering, Covenant University Ota, using Ofite - Reservoir Permeability Tester (RPT), 2015 as shown in Plate 1.The three accumulators in the RPT unit were loaded; the first accumulator was loaded with crude oil, the second was loaded with brine, and the third was loaded with a 25 vol % concentration of the prepared DES. Crude oil was pumped into the core flooding machine at ambient temperature(Orodu et al., 2019) at a rate of 1mL/min until there was no further water flowing from the effluent. The amount of oil stored in the column was measured volumetrically, and the core sample was left in equilibrium at room temperature for 48 hours. After 48 hours of ageing, the core was flooded with brine to simulate real recovery process and achieve residual oil saturation (Sor). The crude oil was extracted until no further oil was observed in the outlet, and the quantity of oil retrieved over time was recorded.

As part of the tertiary recovery operation, a 25 vol % concentration of the DES in the third accumulator was used to flood the core plug in the core holder, the effluent was extracted, and the 'incremental' oil recovered with time was measured.

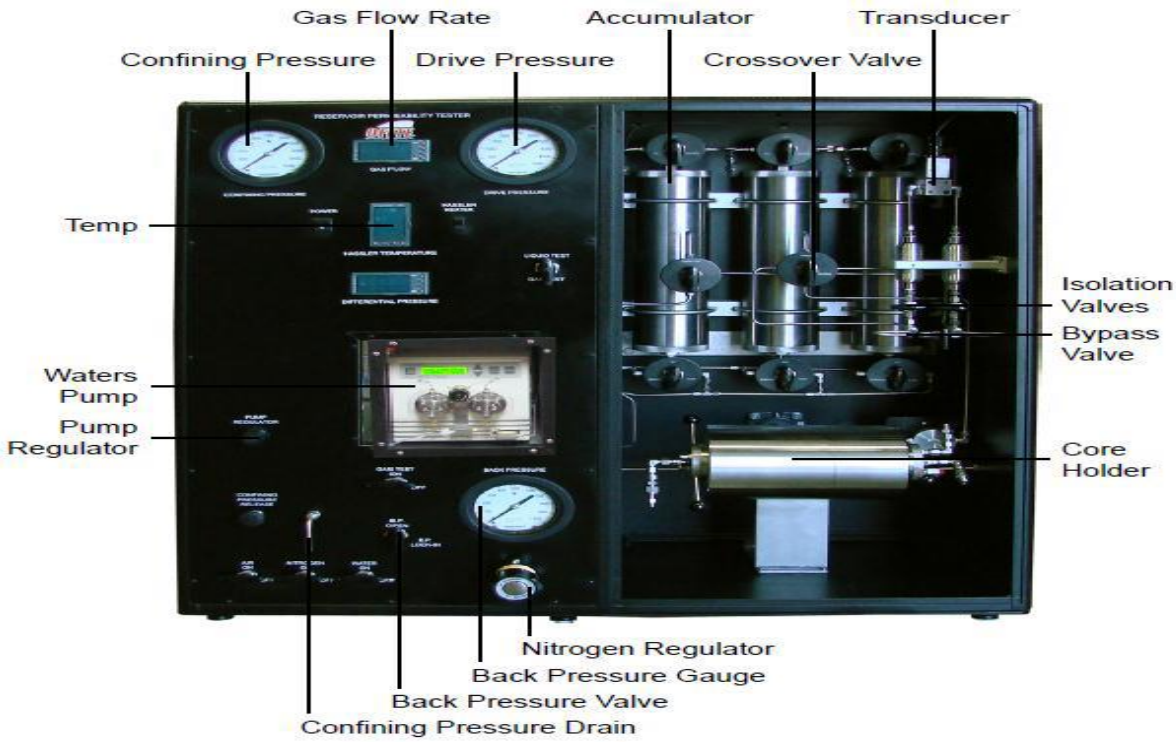


Plate 1: Ofite - Reservoir Permeability Tester, 2015 (Source – Covenant University, Ota)

3. RESULTS AND DISCUSSION

3.1Synthesis and characterization of the DES

DES 1 was successfully synthesized in a 1:2 molar ratio of TBAB and polyethylene glycol 400 (PEG 400), while DES 2 and DES 3 were synthesized in a 1:6 molar ratio of TBAB:DMSO and TBAB:DMF respectively.

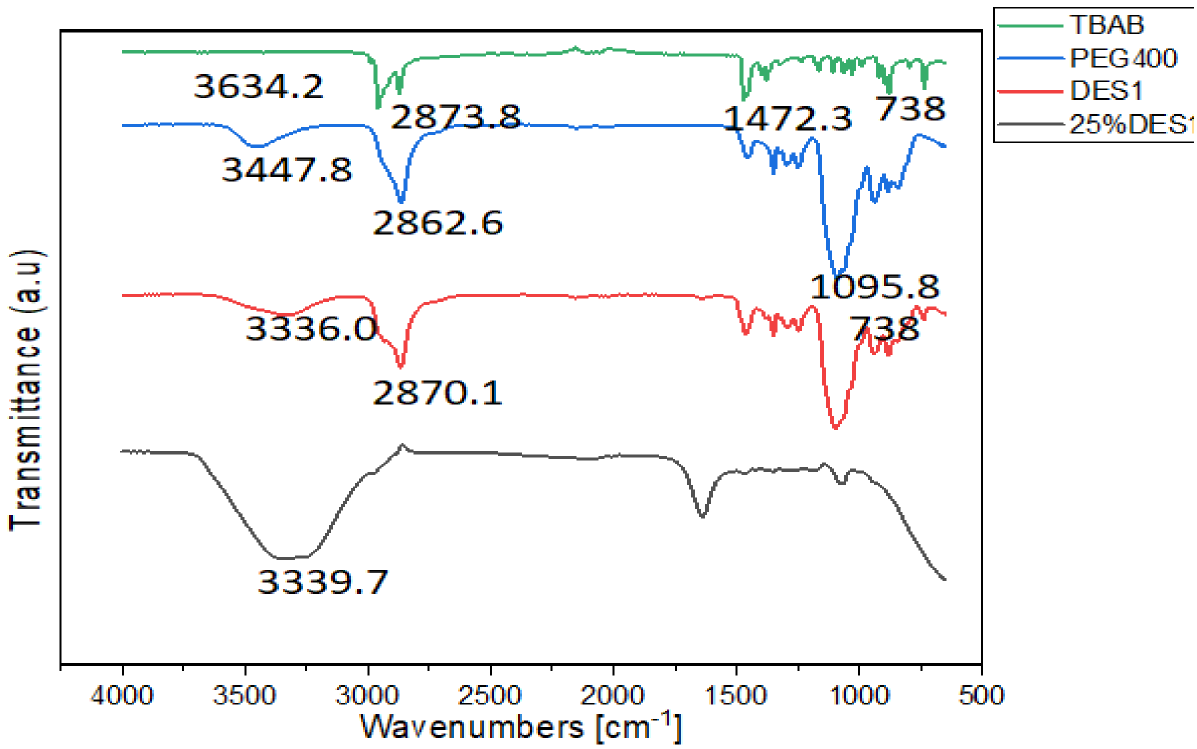
The applicability of DES in interfacial processes involving mass transport is mostly determined by viscosity, density and surface tension(Makoś et al., 2020), while moisture content and refractive index is used to assess the purity of the DES or the concentration of that DES in a matrix (Naser et al., 2013). Table 1 shows the properties of the synthesized DESs (DES 1, DES 2 and DES 3), as well as some of the properties of synthesized DESs in literature (Ijardar, 2020; Xu et al., 2020). Some of the values, such as the viscosity and density of DES 1, are found to be similar to the literature values, which suggest that the produced DES 1 may be similar to some other synthesized DES in literature. Also, Table 1 shows that DES 3 has the lowest density (1.0079g/cm^3) followed by DES 2 (1.0809g/cm^3), which confirms that the density of DESs depends on the components of DES as well as their molar ratio (Sanati et al., 2021). The table also shows that DES 1, which is a mixture of TBAB and PEG 400, has the highest viscosity (198.0mm^2/s) compared to DES 2 and DES 3.This is attributed to the availability of extra hydroxyl groups from PEG 400, which creates more hydrogen bonds and in turn increases the attractive forces between molecules, making DES 1 more viscous than DES 2 and DES 3. As a result, DES 1 may be less efficient in reducing the interfacial tension (IFT) between water and heavy oil, which can reduce residual oil saturation trapped in porous medium after water flooding. Therefore, Wettability alteration as a result of its higher viscosity will be the primary mechanism for oil recovery in DES 1.

Table 1. Physical Properties of DES

Physical property	DES 1	DES 2	DES 3	Literature
Viscosity @ 28.7℃ (mm^2/s)	198.0	17.30	44.3	198.77(Ijardar, 2020)
Density @ 28.7℃ (g/cm^3)	1.1052	1.0809	1.0079	1.1054(Ijardar, 2020)
Surface tension (mN/m)	42.98	35.06	35.86	
Moisture content	0.0242	0.0409	0.0716	0.0618 (Xu et al., 2020)
Refractive index @ 28.7℃	1.4740	1.4845	1.4570	

3.2 FT-IR characterization of the DES

Aside the formation of transparent homogeneous liquids and the physical properties of the synthesized DESs displayed in Table 1, FT-IR spectra were also used to study intermolecular interactions of various tetrabutylammonium bromide based-DESs and 25 v/v % DESs in the brine. In Figure 1, for bromide (TBAB), absorption band at 738cm^{-1} depicts C-Br stretching vibrations, 1472.3 cm^{-1}depicts C-H stretching vibrations of methyl group, 2873.8 cm^{-1}depicts C–H stretching vibrations of sp^3 hybridized, while the absence of a peak at 3634.2 cm^{-1}shows the absence of O-H stretching vibrations. In Figure 1 (a), 2862.6 cm^{-1}depicts C–H stretching vibrations of sp^3 hybridized, 3447.8 cm^{-1}O-H stretching vibrations in polyethylene glycol 400 (PEG 400). While Figure 1 (b) shows1043.7 cm^{-1}S=O stretching vibrations of sulfoxide group in dimethyl sulfoxide (DMSO), and Figure 1 (c) shows 1658.7 cm^{-1} C=O stretching vibrations of amide group, and 3313.6 cm^{-1}, which depicts N-H stretching vibrations of amide group in N,N-dimethyl formamide (DMF).



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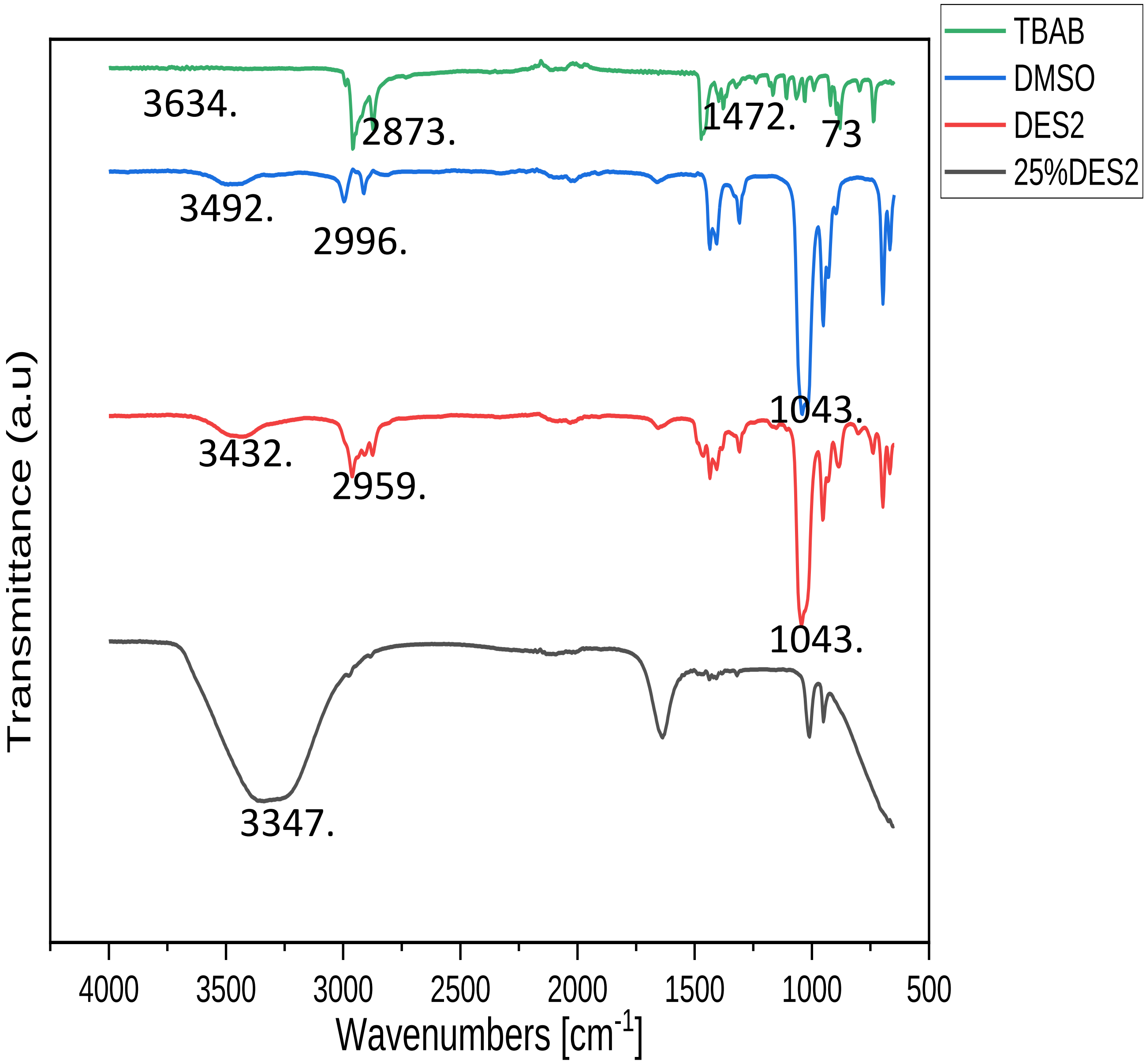

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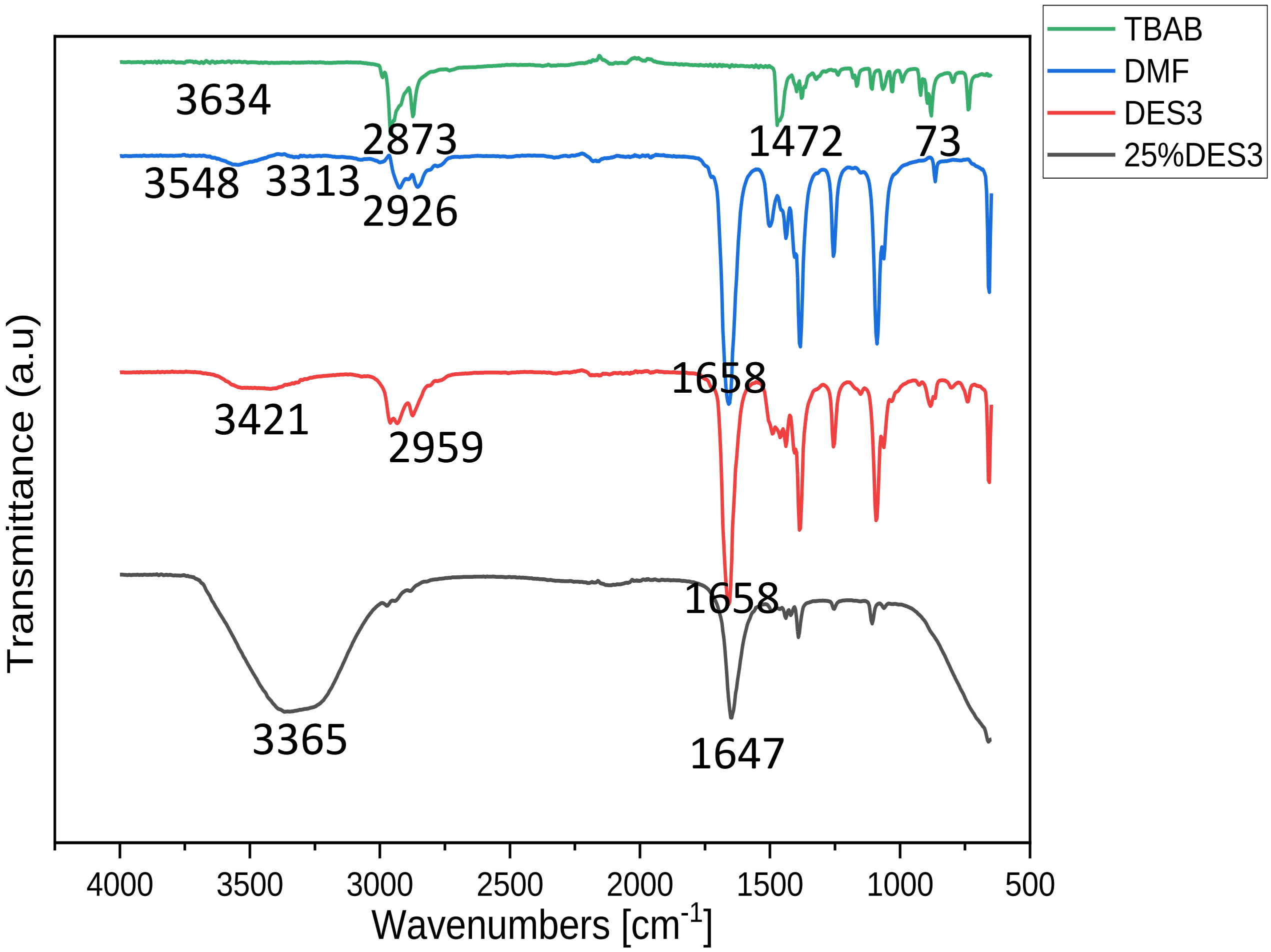

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Figure 1. FT-IR of (a) TBAB, PEG400, DES 1 and dilute DES 1, (b) TBAB, DMF, DES 2 and dilute DES 2, (c) TBAB, DSO, DES 3 and dilute DES 3.

As indicated in Figure 1(a, b and c), DES1 displays absorption band at 3336.0 $cm^{-1}$and DES2 exhibits a peak at 3432.9 cm^{-1} and DES3 depicts a peak at 3421.7 cm^{-1}which indicate O-H stretching vibrations. These show that there are interactions between the components of the DES, which confirm the formation of hydrogen bonding and DES formation, as reported in the literature (El-hoshoudy et al., 2019; Majidi&Hadjmohammadi, 2020; van Osch et al., 2015; Xu et al., 2020). In the three DES formed, there were no new peaks displayed, confirming that formation of DES is a physical process and no chemical reaction takes place. To also confirm the presence of hydrogen bond interaction in 25 v/v % DESs in the brine, FT-IR was carried out. Although there were distortions in peaks of the three DESs, the presence of 3339.7 cm^{-1}, 3347.1 $cm^{-1}$and 3365.8 cm^{-1} in the 25 v/v % DES 1, DES 2 and DES 3 respectively confirm the existence of hydrogen bond interaction and the DES system. However, the hydrogen bond interaction is weakened by the addition of the brine to DES, as stated in literature (Hadj-Kali et al., 2015).

3.3 Core Flooding Test

Core samples were obtained from Berea and Niger-Delta sandstone, and the core flooding test was carried out at ambient temperature. The performance(s) of the three DES on Niger-Delta and the Berea sandstones are shown in Table 2. Core with DES 1has a length of 0.024 m and a diameter of 0.0340 m, with a porosity of 32.11 % and a permeability of 208.5 mD, resulting in an incremental oil recovery of 35.94 % and a very high ultimate recovery of 85.94 %.There was also an incremental oil recovery of 17.14 % using DES 2 from core flooding using Niger-Delta sandstone, while the presence of DES 3 improved the recovery by 19.56% for the Berea sandstones. This demonstrates the potency of DES as a solvent for improved oil recovery.

Table 2.Core flooding experiment

Core sample		Niger-Delta **Core with DES 1**	Niger-Delta **Core with DES 2**	Berea **Core with DES 3**
Core properties	Length (m)	0.0240	0.062	0.024
	Diameter (m)	0.0340	0.032	0.035
	Pore Volume x 10^{-6} (m^3)	7.00	8.0	6.0
	Porosity (%)	32.11	16.04	25.97
	Permeability (mD)	208.5	315.12	211.89
Initial conditions	Initial oil in place, IOIP x10^{-6} (m^3)	6.40	7.0	4.6
	Initial oil saturation S_{oi} (%)	91.43	87.5	76.67
	Initial water saturation S_{wi} (%)	8.57	12.5	23.33
Oil recovery factor based on IOIP (%)	Brine flooding	50.0	44.29	30.43
	25 vol % DES 1 flooding	35.94	17.14	19.56
	Total recovery factor	85.94	61.43	49.99

3.4 Characterization of the crude oil

After flooding with DES, the effluent was taken and the crude oil was separated from the DES using a separating funnel. In order to see the interaction between the heavy oil and the crude oil, FT-IR analysis was carried out. As depicted in Figure 2, there was no formation of new peak, which implies there was only an infinitesimal amount or trace of DES in the oil. Hence, DES is a good solvent for oil recovery as it does not react with oil and it has the potential of upgrading heavy oil, e.g. by decreasing the viscosity of the oil, as shown in Table 3.

Table 3. Physical Properties of crude oil before and after flooding

Physical property	Crude oil before injection	Crude oil after DES 1 injection	Crude oil after DES 2 injection	Crude oil after DES 3 injection
Viscosity @ 28.7°C(mm^2/s)	374.5	366.8	314.6	290.0
Relative Density	0.96	0.94	0.95	0.95
API˚@ 15 °C	15.25	18.27	16.75	16.75
Moisture content (%)	0.0505	0.0348	0.0227	0.0510

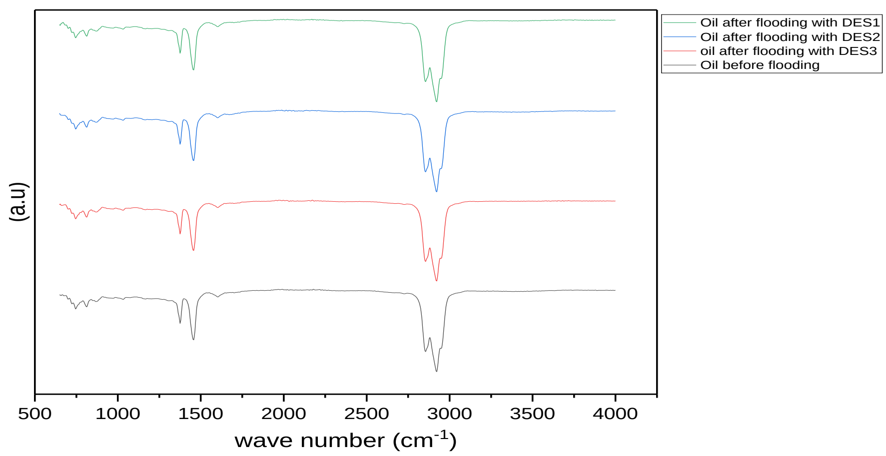

Figure 2. FT-IR of oil before and after flooding with DES

3.5 Interfacial tension reduction test

Figure 3 shows that 25 vol % DES 2 substantially reduces the IFT from 5.19 to 2.46 mN/m, while 25 vol % DES 3 moderately reduces the IFT from 5.19 to 4.29 mN/m. Alternatively, there was an increase in IFT from 5.19 to 6.61 mN/m between the oil/25 v/v% DES 1. It was only after the concentration of DES 1 was increased from 25 v/v% to 27 v/v % that a decrease to 4.34 mN/m was observed. The increase in IFT at 25 and 26 v/v% of DES could be as a result of insufficient DES available to effectively increase the capillary number (Sanati et al., 2021), and/or the higher viscosity of DES 1, as shown in Table 1. Nevertheless, the study confirms that DES has a significant effect on IFT.

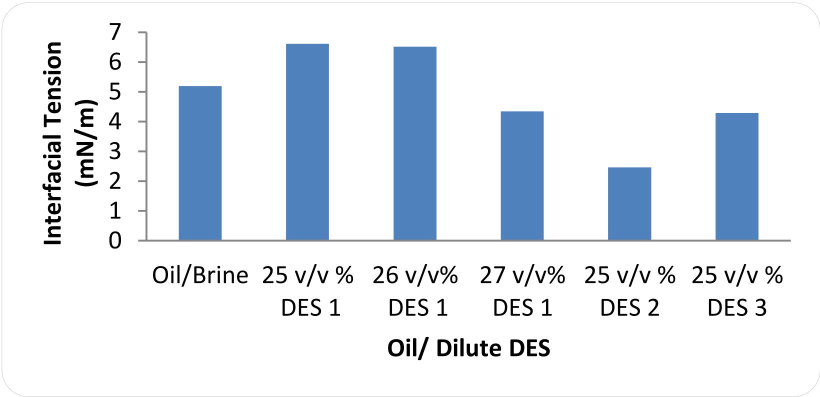

Figure3. Interfacial (IFT) reduction test

4. CONCLUSION

In this study, DES 1 was successfully synthesized in a 1:2 molar ratio of tetrabutylammonium bromide (TBAB) and polyethylene glycol 400 (PEG 400), while DES 2 and DES 3 were successfully synthesized in a 1:6 molar ratio of TBAB/dimethyl sulfoxide (DMS) and TBAB/N,N-dimethyl formamide (DMF) respectively. FT-IR results confirmed the existence of hydrogen bond interaction, and the DES system in 25 v/v % DESs in the brine. The presence of 25 vol % DES 1 led to the recovery of additional35.94%, resulting in a high overall oil recovery of 85.94 %. While an additional recovery of 17.14 % was obtained using DES 2 from core flooding using Niger-Delta sandstone. Similarly, the presence of DES 3 improved the recovery by up to 19.56% for the Berea sandstones. For the recovered oil, FT-IR confirmed that there was no trace of DES in the oil. This study highlights that it was possible to reduce the Interfacial (IFT) between the oil and the DES phase from 5.19 to 2.46 mN/m, showing that DES can significantly reduce IFT. Thus the study confirms that the presence of DES promotes reduction in the viscosity of the heavy Nigerian oil, increase in API gravity, decrease in IFT, and results in enhanced oil recovery.

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