

Application of deep eutectic solvents and their individual constituents as surfactants for enhanced oil recovery



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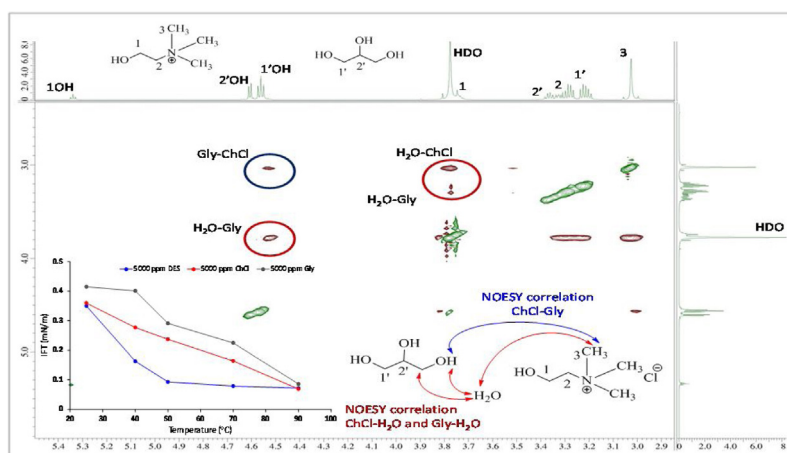
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HIGHLIGHTS

- IFT of crude oil-brine system was measured in the presence of selected DESs.
- The IFT decreases with increasing temperature and DES concentration.
- DES or its constituents affect the IFT similarly and are potential surfactants.
- Molecular interactions in DESs were examined by ¹H NMR and 2D NMR analysis.
- The addition of more than 25 wt% H₂O breaks the DES' hydrogen bonds.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 26 June 2015

Received in revised form

29 September 2015

Accepted 5 October 2015

Available online 9 October 2015

Keywords:

Deep eutectic solvents

Interfacial tension

Surfactants

Enhanced oil recovery

ABSTRACT

We investigated the potential use of choline chloride/urea and choline chloride/glycerol deep eutectic solvents (DESs) and their individual constituents (the salt and the hydrogen bond donor) as surfactants for enhanced oil recovery. The interfacial tension (IFT) between Saudi medium crude oil and different concentrations of these DESs (and their individual components) in 10 wt% NaCl aqueous solutions were measured as a function of temperature. Results showed that the IFT values decreased with the increase of both the DES concentration and temperature. The effect of adding the salt and the hydrogen bond donor (HBD) separately, without forming the corresponding DES, on IFT values was also explored. It was found that, in most cases, adding the DES or its corresponding constituents separately has the same effect on the IFT. Furthermore, ¹H NMR and different 2D NMR analysis (NOESY and HOESY) were used to examine the nature of molecular interactions that occur in studied DESs and how water affects these interactions. It was found that while the content of water is below 25 wt% the interactions of DES' components become weak. However, the addition of 50 wt% water breaks the hydrogen bonding so that no interactions between the HBD and the salt were observed.

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Abbreviations: AMNS, alkylmethylnaphthalene sulfonates; BTBAC, benzyltributylammonium chloride; BTMAC, benzyltrimethylammonium chloride; ChCl, choline chloride; CTAB, cetyltrimethylammonium bromide; DES1, ChCl:glycerol (1:3); DES2, ChCl:urea (1:2); DESs, deep eutectic solvents; EOR, enhanced oil recovery; HPAM, hydrolyzed polyacrylamide; IFT, interfacial tension; ILs, ionic liquids; MTPPBBr, methyltriphenylphosphonium bromide.

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<http://dx.doi.org/10.1016/j.colsurfa.2015.10.005>

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1. Introduction

The appetite for global energy is increasing steadily due to rapid growth in world's population. Rising energy demand becomes the main reason for applying different technologies to improve the efficiency of petroleum production [1]. The laboratory and field study revealed that only 30–50% of oil can be recovered after water injection from original oil in place [2]. To extract remaining oil, it is necessary to incorporate efficient techniques. Enhanced oil recovery (EOR), also called tertiary oil recovery, is the one gaining more interest [3].

There are three major techniques for EOR: (i) thermal recovery, (ii) gas and (iii) chemical injections [4]. (i) Thermal recovery methods are generally used to recover viscous and heavy oil. In such methods, thermal energy is injected into the reservoir to raise its temperature [5]. The major aim of such techniques is to reduce the viscosity of crude oil and thereby improve its mobility within the reservoir. The common thermal recovery methods include in-situ combustion, hot fluid injection and cyclic steam [6]. (ii) The gas injection technique consists of pumping different hydrocarbon or non-hydrocarbon gases into reservoirs [7,8]. Injected gases typically include nitrogen, carbon dioxide or natural gas. (iii) Chemical flooding techniques are considered as the best EOR techniques used [7,9–12]. They could be divided into three main processes: (a) alkaline flooding, (b) polymer flooding and (c) surfactant flooding [2]. Alkaline flooding method is not as efficient as other techniques; although, it is the cheapest one [13]. The relative lower capital cost has made the polymer flooding one of the most attractive EOR processes for the researchers in recent years [14]. In this technique, water-to-oil mobility ratio is reduced by employing polymers in order to guarantee the considerable oil displacement front.

Among several chemical EOR methods, surfactants represent an important class to recover crude oil [2,7,15–17]. In this technique, the residual oil mobility is enhanced through reduction in interfacial tension (IFT) by introducing a surface active agent (surfactant) [18,19]. Moreover, the reduced IFT between oil and water lowers the capillary pressure and thereby improves the sweep as well as displacement efficiency [20]. The oil characteristics as well as, the reservoirs' conditions play a significant role in selecting the suitable surfactant [21–28]. As a rule, increasing the electrolyte concentration will result in greater adsorption and a lower IFT of an ionic surfactant even at the air/water interface. This is due to a decrease in Debye screening length with increasing electrolyte concentration.

In 2008, Gong et al. [29] measured the dynamic IFT between hydrolyzed polyacrylamide (HPAM)/sodium oleate ($C_{17}H_{33}COONa$) solution and crude oil. They studied the effects of sodium halide (NaF, NaBr, NaCl or NaI) on the dynamic IFT and the viscosity of the mixed solution. Results showed that the IFT can be reduced to 10^{-4} mN/m in a very short period of time. It was also found that among different precipitants of sodium halide, the reduction in the IFT between HPAM/ $C_{17}H_{33}COONa$ solution and crude oil is more dominant in the presence of NaI. Zhang et al. [30] synthesized hydrophobic modified sodium humate surfactants (C_n -HANa) with varying chain lengths. The experimental spinning drop analysis results revealed that ultra-low IFT value was achieved at the oil/water interface from the solution of *n*-propanol, $Na_3PO_4 \cdot 12H_2O$ and the surfactant. Ko et al. [15] investigated the phase behavior of dodecyl alkyl sulfate and selected crude oil samples. They studied the effects of branched and linear dodecyl alkyl sulfate and reported that the branched chain surfactant was more efficient than the linear surfactant. They used both light and heavy crude oils with various salinity concentrations during the phase behavior test.

Microemulsion systems can also be used to attain the ultra-low IFT between crude oil and water. Bera et al. [31] measured the IFT between surfactant solutions, oil and brine and microemul-

sion, and showed that microemulsion system has substantial role in reducing the IFT. The effect of alkylmethylnaphthalene sulfonates (AMNS) based surfactants on the dynamic IFT between crude oil and the solution of surfactants and the surface tension of surfactant aqueous solution was investigated by Zhao et al. [32]. They found that these surfactants have great potential in lowering the surface tension and IFT values and become more efficient in the presence of NaCl. A mixture of polyoxyethylene *tert*-octylphenyl ether (TX-100) and Tyloxapol in brine solution and in the presence of HPAM with cetyltrimethylammonium bromide (CTAB) was analyzed at the interface between crude oil and water by Zhu et al. [33]. Results showed that CTAB has better capability and efficiency in reducing IFT compared to the nonionic surfactant. It is also worth mentioning here that all surfactant mixtures yield ultra-low IFT values in the presence of HPAM.

Several publications have been reported in the last decade that investigated the influence of ionic liquids (ILs) on the IFT of crude oil/water system [2]. Benzagouta et al. [2] used a special class of ILs called "Ammonoeng" as a surfactant for the applications of EOR. They investigated the effects of these ILs on the IFT in the presence of NaCl solution as a function of temperature. Results showed that the increase in the concentration of ILs causes reduction in the IFT values. The lowest IFT values were achieved by using Ammonoeng 102 IL (tetraalkyl ammonium sulfate) which gave lower IFT values than the commercial surfactant: Triton X-100. The authors also studied the synergic effect of using a mixture of Triton X-100 and Ammonoeng 102 and they found that the total concentration of surfactant and IL, the temperature and the mass ratio of surfactant to IL play a major role in decreasing the IFT.

Hezave et al. [3] used 1-dodecyl-3-methylimidazolium chloride ($[C_{12}mim-Cl]$) IL as a surfactant for EOR. They performed a parametric analysis by investigating the effects of NaCl solutions, salinity, temperature and concentration of IL on dynamic IFT between IL solution (water + IL) and heavy crude oil. It was found that the increase in temperature reduces IFT of the ILs solution/crude oil system. Sakthivel et al. [34] used eight aliphatic ILs for the investigation of IFT between crude oil and water and surface tension of water. The synergic effect of ILs in the presence of NaCl was also examined. Both IFT of oil/water system and surface tension of water decreased in the presence of NaCl, as well as by increasing the temperature, the ILs' concentration and the alkyl chain length of the cation of the IL. The effect of two different families of ILs, namely pyridinium and imidazolium on the IFT of crude oil/water system was investigated by Hezave et al. [35]. In their study, they used four ILs including 1-dodecyl-3-methylimidazolium chloride ($[C_{12}min][Cl]$), 1-octyl-3-methylimidazolium chloride ($[C_8min][Cl]$), 1-dodecyl pyridinium chloride ($[C_{12}Py][Cl]$) and 1-octyl pyridinium chloride ($[C_8Py][Cl]$). They studied the influence of temperature and concentration of NaCl and ILs on IFT values, and they revealed that, unlike conventional surfactants, these four ILs are more efficient in the presence of NaCl to reduce the IFT.

Some researchers have also used different ammonium and phosphonium salts as surfactants to reduce IFT. Wei et al. [36] measured the dynamic interfacial tension (DIT) between *n*-octane and aqueous solution of 3-alkoxy-2-hydroxypropyl-trimethyl ammonium chloride (R_nHTAC) by using a spinning drop method. Their study revealed that the increase in the concentration of surfactant reduces the DIT. Fu et al. [37] also used the spinning drop method to measure the DIT between aqueous solutions of *n*-hexane and 3-dodecyloxy-2-hydroxypropyl trimethyl ammonium bromide ($R_{12}HTAB$). The results showed that the DIT decreases and adsorption barrier gets higher in the bulk aqueous phase with increasing the concentration of surfactant while the increase in the temperature of the solution reduces the DIT. Lim et al. [38] studied the influence of cationic surfactants having multi ammonium and hydroxyl groups on the dynamic surface tension and IFT. It

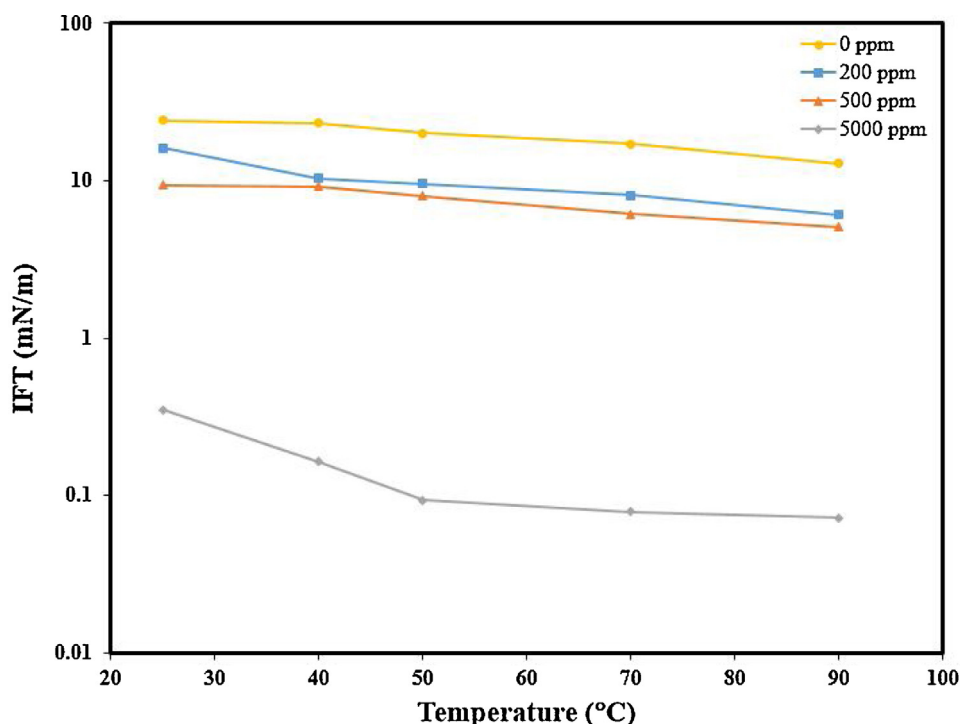


Fig. 1. IFT as a function of temperature for DES1 having different concentrations in 10 wt% NaCl solution and Saudi medium oil.

was reported that the critical micelle concentration of the aqueous surfactant solution increases by increasing the hydrophobicity of a surfactant. Very low values of surface tension were achieved by using cationic surfactant, which consists of a mono-ammonium group and two hydroxyl groups. A maximum bubble pressure tensiometer was used to measure the dynamic surface tension. IFT was measured between *n*-decane oil and 1 wt% surfactant solution at 25 °C using a spinning drop tensiometer. The IFT dropped to an equilibrium value over a time period of about 10–15 min. For example, the equilibrium value of *N,N*-bis-(3-(3-*n*-dodecyloxy-2-hydroxypropyl)-*N,N*-dimethylammonium)-2 hydroxypropyl dimethyl ammonium dichloride methyl sulfate was 0.162 mN/m. Theoretical and experimental studies were performed by Pons-Jiménez et al. [39] to investigate the influence of the cationic surfactant docetyltrimethylammonium chloride (C_{12} TAC) on the enhancement of the oil recovery factor (ORF). They determined interaction energies between C_{12} TAC and the fractions present in heavy oil. This theoretical analysis was based on Density Functional Theory. They observed the reduction of oil viscosity from the molecular interactions between C_{12} TAC and either of some molecules present in oil. Based on experimental analysis, Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR) spectra were performed on the heavy crude oil. Due to the addition of C_{12} TAC surfactant into the brine solution, a noticeable increase in the ORF was observed. Müller and Dörfler [40] studied adsorption and inhibition behavior of homologous phosphonium bromides using different techniques. The experiments were carried out in ethanol/water solutions. Results showed that the inclusion of homologous phosphonium bromides in ethanol/water solutions causes reduction in the IFT values between homologous phosphonium bromides and ethanol/water electrolytic solutions. Finally, Kang et al. [41] prepared cationic surfactants having two hydrophobic groups and two quaternary ammonium ions. FTIR, HNMR and fast atom bombardment mass spectrometry techniques were utilized for the characterization purpose of the surfactants. The interfacial properties including critical micelle concentration, sur-

face tension, and interfacial tension between oil and surfactant solution, foam stability and contact angle were measured.

Nevertheless, the huge market demand for surfactants is currently satisfied by synthetic petroleum-based chemicals which may bio-accumulate and which by-products and production processes can be environmentally hazardous [42]. However, due to the environmental issues and restrictive laws, biodegradable and non-toxic surfactants are inevitable. In addition, it is well known that surfactant systems are sensitive to high temperatures and high salinity, leading to requirements for developing surfactant systems that can withstand such conditions [25].

DESs are a low-cost alternative of ILs and have emerged as new generation of green solvents. A DES is obtained by mixing a complexing agent (generally a hydrogen bond donor) with a salt at a specific molar ratio forming a eutectic with a melting point lower than that of each individual component. Depression of freezing point is related to the interaction between the components of the mixture, generally of hydrogen bonding nature. The salt used for the synthesis of DESs consists of a large quaternary ammonium or phosphonium cation, combined with a halide anion. An example of a common DES is the combination of choline chloride (ChCl) with urea, which forms a eutectic mixture when 1 mole of ChCl is mixed with 2 moles of urea [43]. In addition to be non-volatile, DESs have several advantages compared to traditional ionic liquids since they are: (1) simple to synthesize; the materials can be easily mixed and ready to be used without further purification, (2) less expensive, and (3) are generally biodegradable and non-toxic based on the wise choice of their constituents [44]. Mohsenzadeh et al. investigated the effectiveness of choline chloride: glycerol (1:2) and choline chloride: urea (1:2) DESs in enhancing Omani heavy oil recovery [45]. Effects of the two DESs diluted with brine on emulsification, wettability, spontaneous imbibition, surface and interfacial tensions were reported at different temperatures. The results showed that the two DESs increased the IFT of oil-brine system. In addition, the two DESs altered the wettability of the sandstone rock surfaces from liquid-wetting towards intermediately air-wetting conditions at oil-air-rock interface. The core

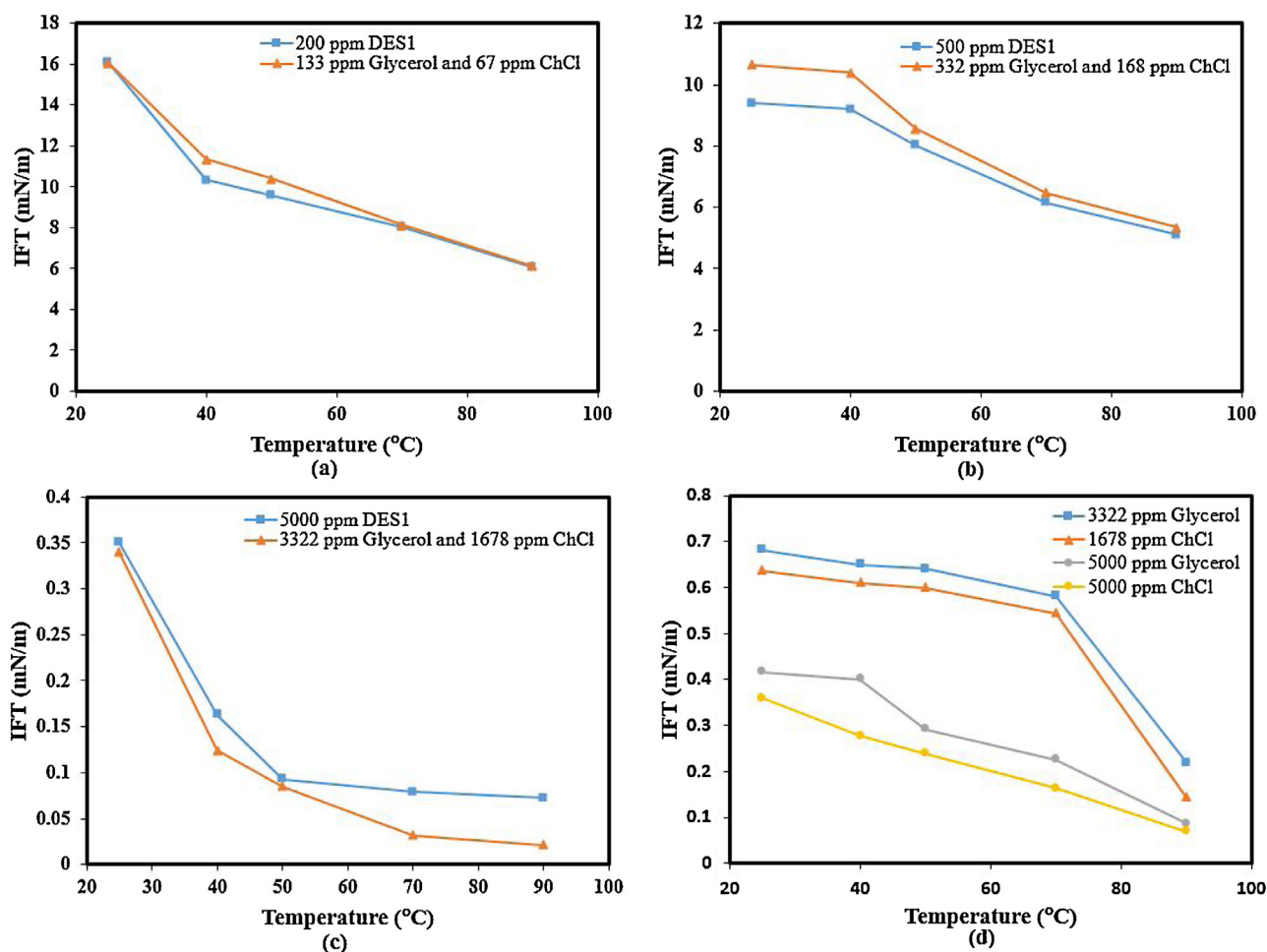


Fig. 2. IFT comparison between DES1 and its components (added separately) in 10 wt% NaCl brine solution and medium crude oil at different temperatures.

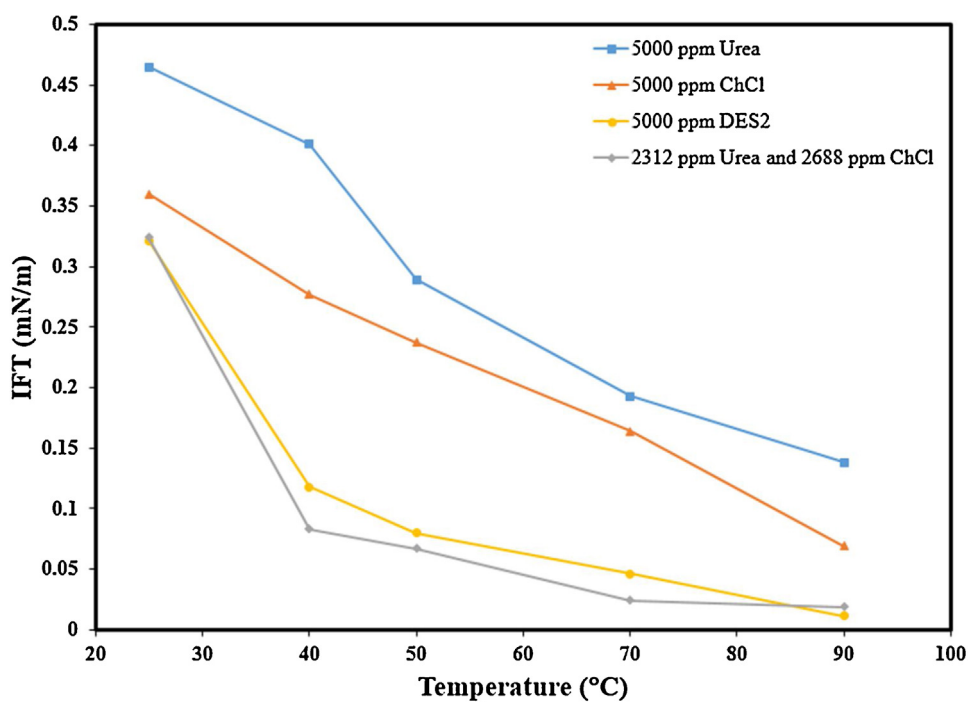


Fig. 3. IFT measurement of DES2 and its components in 10 wt% NaCl brine and Saudi medium oil at different temperatures.

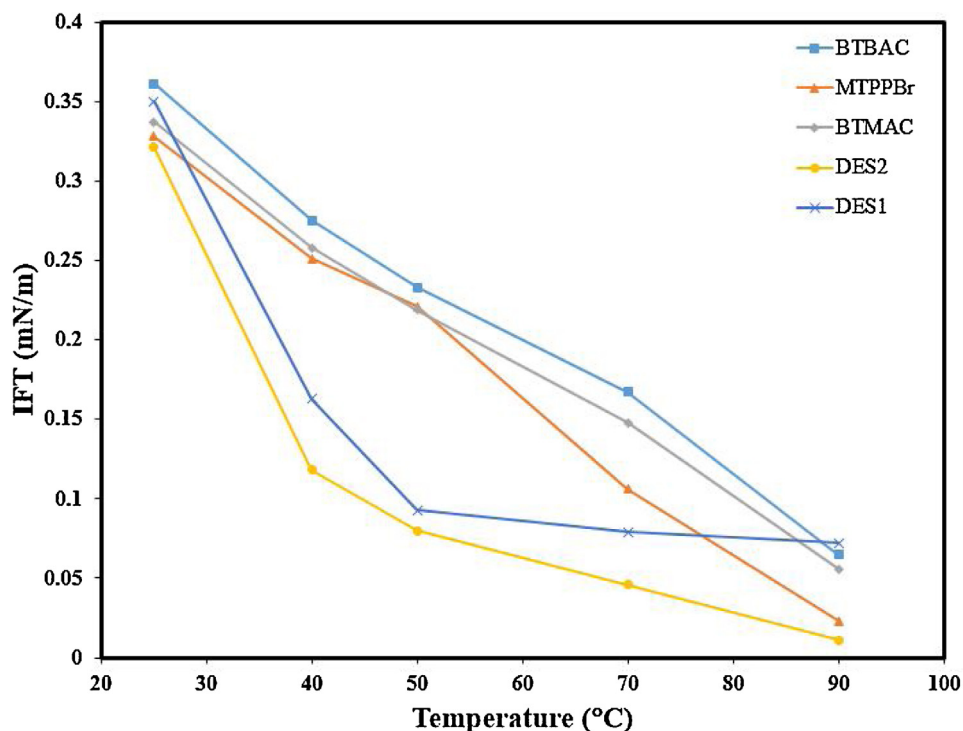


Fig. 4. IFT comparison of 5000 ppm DESs and selected salts having 10 wt% NaCl solution and medium Saudi oil at different temperatures.

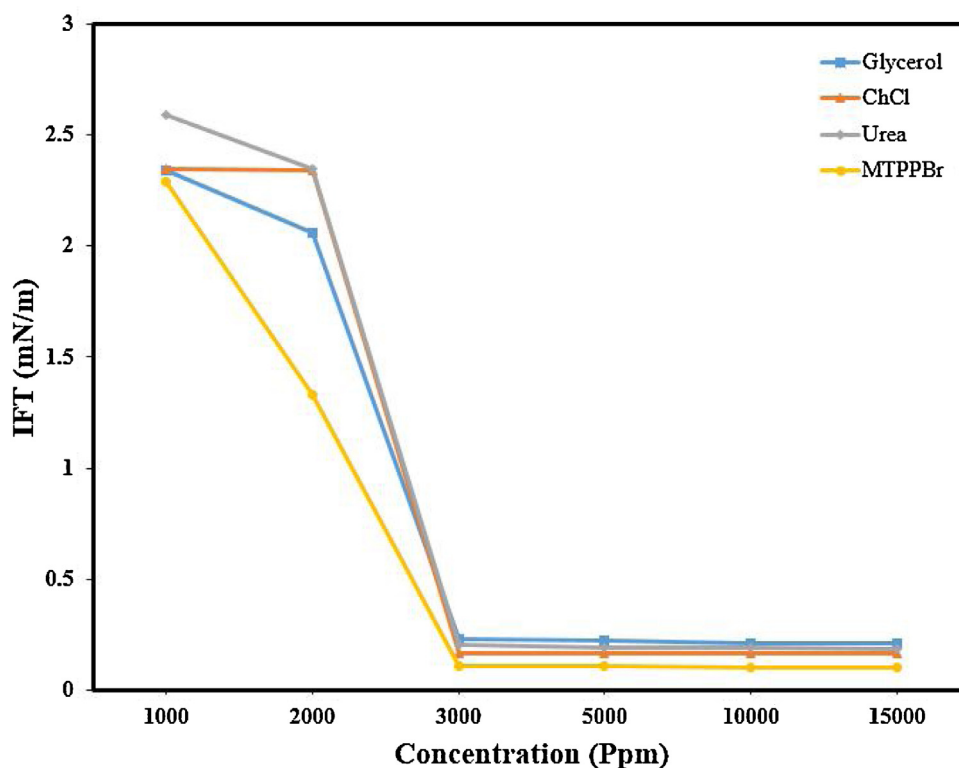


Fig. 5. Effect of the salt or hydrogen bond donors' concentration in 10 wt% NaCl aqueous solution on the IFT with Saudi medium oil at 70 °C.

flooding runs at different temperatures showed high potential of using these DESs for enhancing heavy oil recovery. They concluded that wettability alteration and reduction of viscous forces were the main mechanisms of enhancing the heavy oil recovery by DESs injection. It should be noted that Mohsenzadeh et al. used 50 vol%

of DES which is an extremely high concentration compared to the values reported in the literature for other surfactants.

In the present work, the potential application of selected deep eutectic solvents and their individual components as surfactants was investigated. The IFT behavior between crude oil/brine and two

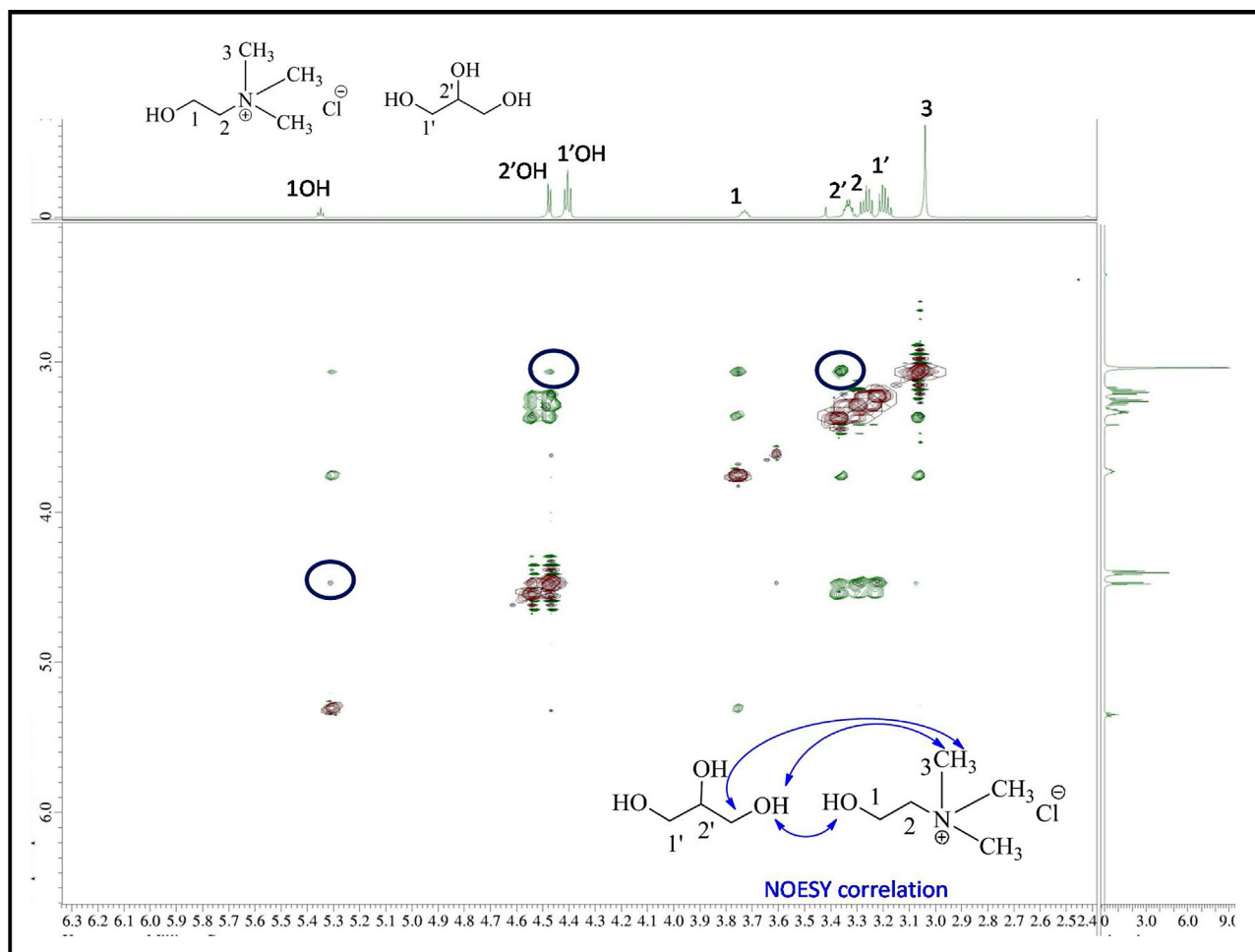


Fig. 6. 2D NMR spectra of ChCl:glycerol (1:3): ^1H – ^1H -nuclear overhauser enhancement spectroscopy (NOESY) in DMSO.

different DESs was measured at atmospheric pressure and different temperatures and concentrations.

2. Materials and methods

Pure grade compounds sodium chloride and choline chloride were purchased from Acros Organics (Belgium), urea from Winlab (England) and glycerol from Panreac (Spain) and were of 99% purity. All chemicals were used without any further purification.

Two different DESs: ChCl:glycerol (1:3) and ChCl:urea (1:2) were prepared according to the method described by Abbot et al. [43]. These are denoted as DES1 and DES2, respectively. ChCl was mixed with the hydrogen bond donor (Urea or glycerol) in screw-capped bottles. The bottles were then placed in an incubating-shaker at a temperature of 100 °C and a rotational speed of 200 rpm until a clear liquid was formed.

10 wt% NaCl solution in deionized water was used to represent the typical condition of brine which exists in most petroleum reservoirs in Saudi Arabia. The unit used for the concentration of the DESs, the salt solution or the surfactant is ppm, based on weight of materials used. The Saudi medium crude oil used in this work was characterized by determining its viscosity (12 cP) and specific gravity (0.886). All the parameters were measured at King Abdul-Aziz City for Sciences and Technology (KACST). PerkinElmer 2400 series II CHNS/O Analyzer was used to measure the composition of the sample: hydrogen = 9.13 wt%, carbon = 81.29 wt%, nitrogen = 0.70 wt% and sulfur = 2.56 wt%.

Table 1

IFT measurements for selected binary systems: Comparison between our results and data published in the literature [46].

	Temperature (°C)					
	25		35		45	
Benzene–water	This work	[46]	This work	[46]	This work	[46]
	29.08 ₁₈	32.50	26.52 ₁₄	31.14	25.87 ₇	29.74
Toluene–water	This work	[46]	This work	[46]	This work	[46]
	36.64 ₁	34.62	35.98 ₃	33.39	34.90 ₁	32.16

The IFT measurements were taken using Kruss Pendant Drop apparatus DSA100 (Germany). The reported accuracy of the measured IFT is ± 0.01 mN/m. This equipment is capable of measuring surface tension and IFT at various conditions of pressure and temperature. To test the equipment and procedure used, IFT values between water and three standard hydrocarbons (*n*-hexane, benzene and toluene) were measured at three different temperatures (25, 35 and 45 °C). Good agreement was obtained between our measurements and those reported in the literature [46] as shown in Table 1. Subscript numbers represent the experimental uncertainties (for example 29.08₁₈ means 29.08 ± 0.18).

Moreover, in order to highlight molecular interactions involved in the DES in the presence of water, nuclear magnetic resonance spectroscopy (NMR) was used. ^1H NMR spectra, 2D NOESY and HOESY spectra were recorded using a JEOL RESONANCE spectrometer ECX-500 II. Dimethyl sulfoxide (DMSO) was used as solvent. The ChCl:glycerol (1:3) DES was prepared and then water was added. A

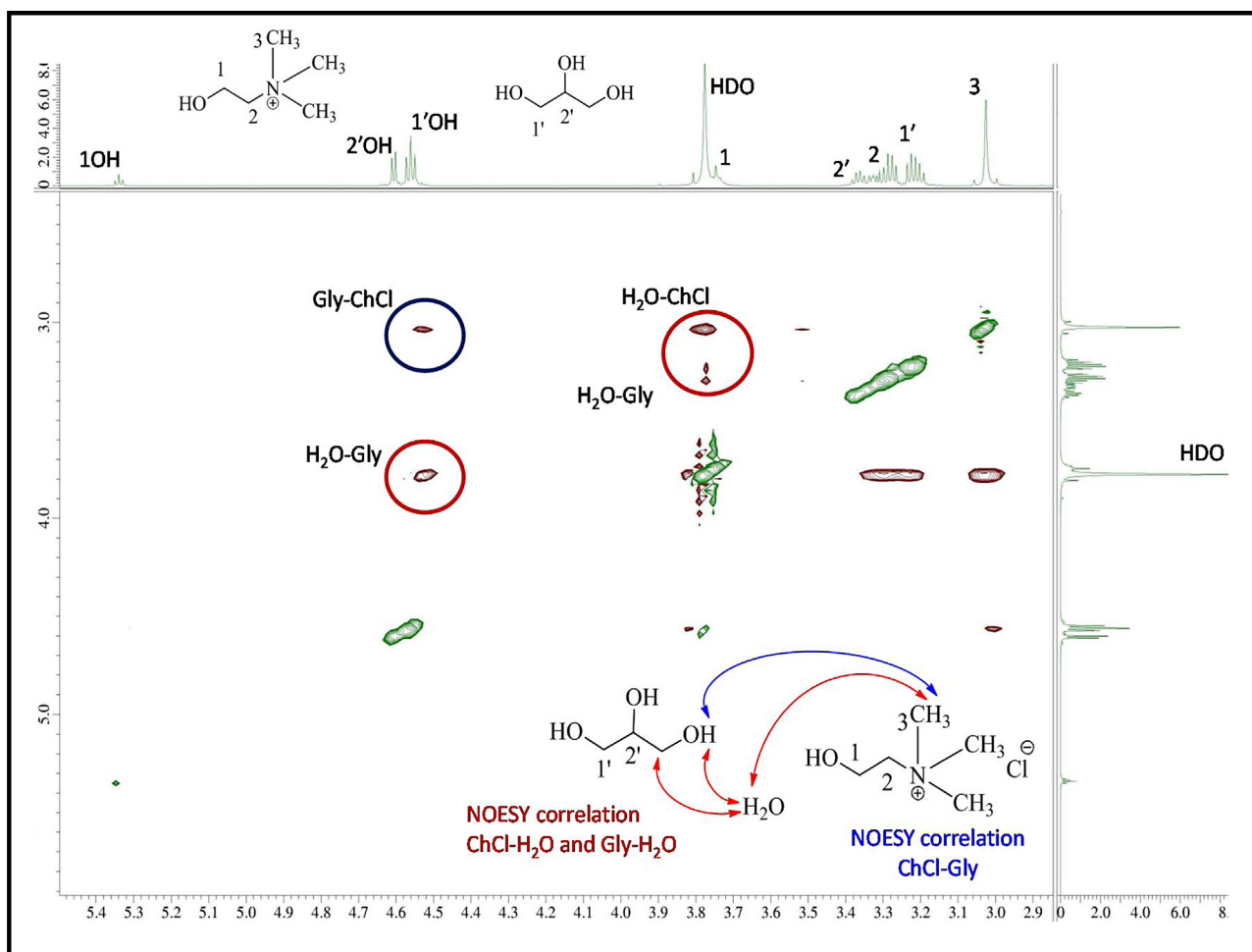


Fig. 7. 2D NMR spectra of ChCl:glycerol:water (1:3:25 wt%): ^1H - ^1H -nuclear overhauser enhancement spectroscopy (NOESY) in DMSO.

Table 2
Density (g/cm^3) of studied DESs at different temperatures.

	Temperature ($^{\circ}\text{C}$)						
	25	40	50	60	70	80	90
DES1	1.2003	1.1919	1.1862	1.1806	1.1781	1.1724	1.1669
DES2	1.2010	1.1928	1.1873	1.1820	1.1738	1.1686	1.1634
Brine	1.0680	1.0616	1.0561	–	1.0455	–	1.0319

sample of 40 mg was diluted in 1 mL of NMR solvent. The spectrums were carried out at 24°C .

3. Results and discussion

The IFT behavior for medium crude oil/brine with two different DESs, ChCl:urea (1:2) and ChCl:glycerol (1:3) was investigated. The IFT measurements were conducted at atmospheric pressure and different temperatures. Table 2 lists the density of the two DESs at different temperatures. As expected, the density decreases with increasing temperature at a constant composition. It could be clearly seen that there is a good agreement between the density values reported here and that published in the literature [47,48].

Fig. 1 illustrates the effect of temperature and composition on IFT for solutions of DES1 (ChCl:glycerol (1:3)) in 10 wt% NaCl brine solution and medium Saudi crude oil. It is clear from the figure that the IFT decreases with the increase of DES concentration. Brine/medium crude oil mixture gives higher values of IFT without any DES as surfactant, reaches up to 24.11 mN/m as shown in

the figure. With the addition of only 5000 ppm DES1, the IFT value decreases to as low as 0.072 mN/m. Moreover, increasing the temperature causes additional reduction in the IFT. Similar results were reported by Shahbaz et al. [49], Ye et al. [50] and Hezave et al. [3]. The effect of temperature is attributed to the fact that the viscosity of crude oil reduces drastically as the temperature increases from 25°C to 90°C . In addition, the rise in temperature causes a reduction in the cohesive forces between molecules at the interface resulting in a lower intrinsic liquid/air interfacial tension. IFT reduction is important in chemical EOR because it enhances oil production by reducing the capillary forces. Zhang et al. reported that large amount of oil is trapped in the reservoirs due to the capillary forces [51].

In order to check if the reduction in IFT is due to the presence of the DES or because of its constituents, i.e., choline chloride and glycerol, we investigated the effect of the addition of choline chloride and glycerol without forming a DES on the IFT of brine solution (10,000 ppm NaCl) and medium Saudi oil. The results are shown in Fig. 2 and Table 3. Again, subscripts represent the experimental uncertainties, for example, $24.110_{30} = 24.110 \pm 0.030$. The common behavior in all cases in Fig. 2 is that the IFT values decrease with increasing temperature. Fig. 2(a) and (b) illustrate that DES1 gives slightly smaller values of IFT as compared to the individual components at lower concentrations. However, at higher concentrations, individual components (ChCl and glycerol) yields lower IFT values, Fig. 2(c). Fig. 2(d) shows IFT values for solutions of pure ChCl and glycerol in brine/crude oil system at different concentrations. Fig. 2(d) shows that IFT for pure ChCl having concentration

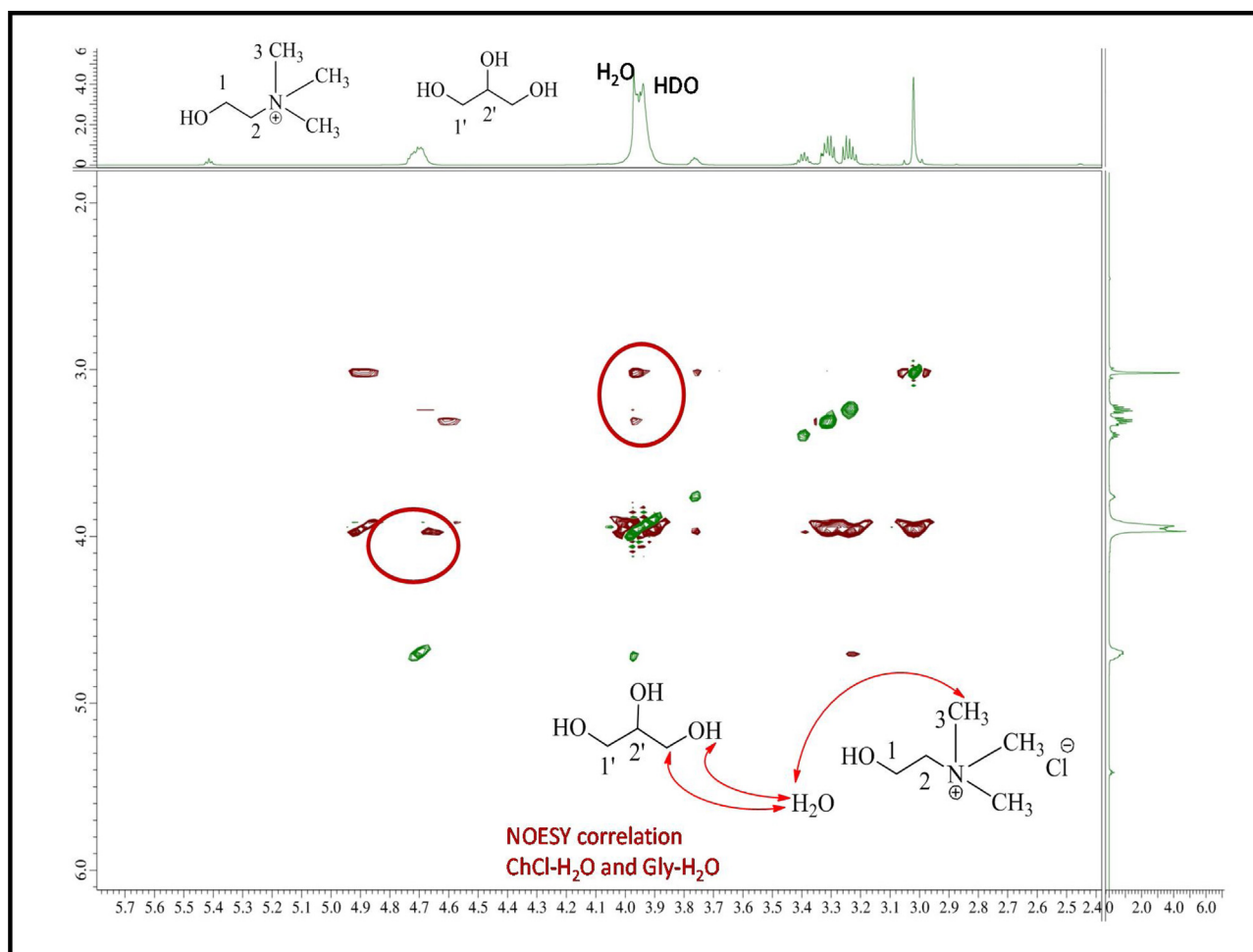


Fig. 8. 2D NMR spectra of ChCl:glycerol:water (1:3:50 wt%): ^1H - ^1H -nuclear overhauser enhancement spectroscopy (NOESY) in DMSO.

Table 3

Comparison of IFT (mN/m) between 5000 ppm aqueous solution of DES1 and the equivalent of ChCl and glycerol in 10 wt.% NaCl and Saudi medium crude oil.

	Temperature (°C)				
	25	40	50	70	90
Brine (10 wt%)	24.110 ₃₀	23.250 ₄₀	20.110 ₃₀	17.080 ₅₀	12.930 ₁₀
DES1 (200 ppm)	16.100 ₄₀	10.320 ₁₀	9.560 ₂₀	8.040 ₂₀	6.060 ₄₀
Glycerol (133 ppm) and ChCl (67 ppm) ^a	16.060 ₁	11.350 ₂₀	10.380 ₃₀	8.120 ₂₀	6.120 ₂₀
DES1 (500 ppm)	9.400 ₂₀	9.190 ₃₀	8.020 ₁	6.140 ₃₀	5.100 ₈₀
Glycerol (332 ppm) and ChCl (168 ppm) ^a	10.640 ₂₀	10.380 ₁	8.560 ₁	6.470 ₅₀	5.340 ₃₀
DES1 (5000 ppm)	0.350 ₁	0.163 ₁	0.0930 ₃	0.0790 ₃	0.072 ₂
Glycerol (3322 ppm) and ChCl (1678 ppm) ^a	0.339 ₁	0.124 ₁	0.084 ₁	0.031 ₇	0.021 ₁
Glycerol (3322 ppm)	0.680 ₂	0.650 ₁₄	0.640 ₅	0.580 ₃	0.220 ₁
ChCl (1678 ppm)	0.637 ₁	0.608 ₁	0.599 ₁	0.544 ₆	0.143 ₄
Glycerol (5000 ppm)	0.415 ₁	0.401 ₁	0.291 ₁	0.225 ₁	0.086 ₇
ChCl (5000 ppm)	0.360 ₁	0.277 ₅	0.237 ₂	0.164 ₂	0.069 ₁

^a The salts and the hydrogen bond donors were added separately.

5000 ppm in brine/oil mixture is much smaller than that for any other pure component.

Then, we have applied the same test with DES2 but only for a total concentration equal to 5000 ppm. Indeed, Fig. 3 depicts IFT behavior of DES2 and its components at different temperatures in 10 wt% NaCl brine and medium Saudi crude oil. The lowest values of IFT were achieved by using 5000 ppm DES2 or when its components, choline chloride and urea, were added separately with total concentration of 5000 ppm and in the same molar ratio in the DES, i.e., 1:2. It can be clearly seen that the decrease in IFT in the two cases is approximately the same. This prompted us to investigate the effect of different salts and different complexing agents

and hydrogen bond donors on the IFT when used separately, i.e., without forming a DES. Table 4 illustrates that the IFT (mN/m) between 5000 ppm aqueous solution of DES2 in 10 wt% NaCl and Saudi medium crude oil was 0.321 mN/m at 25 °C and reduced to 0.011 mN/m by increasing the temperature to 90 °C.

At the same time, we have also examined the effect of other ammonium- and phosphonium-base salts, namely benzyltributylammonium chloride (BTBAC), benzyltrimethylammonium chloride (BTMAC) and methyltriphenylphosphonium bromide (MTTPBr), on the IFT values between 10 wt% NaCl solution and Saudi medium crude oil. The concentration of the salt in each case was taken equal to 5000 ppm. The results are illustrated in

Table 4

Comparison of IFT (mN/m) between 5000 ppm solution of DES2 and the equivalent of ChCl and urea in 10 wt% NaCl brine and Saudi medium crude oil.

	Temperature (°C)				
	25	40	50	70	90
DES2 (5000 ppm)	0.321 ₁	0.118 ₁	0.080 ₀	0.046 ₂	0.011 ₀
Urea (5000 ppm)	0.465 ₂	0.401 ₁	0.289 ₂	0.193 ₁	0.138 ₁₅
ChCl (5000 ppm)	0.360 ₂	0.277 ₅	0.237 ₂	0.164 ₂	0.069 ₁
Urea (2312 ppm) and ChCl (2688 ppm) ^a	0.324 ₁	0.083 ₁	0.067 ₄	0.024 ₃	0.019 ₁

^a The salts and the hydrogen bond donors were added separately.**Table 5**

Comparison of IFT (mN/m) between ammonium and phosphonium salts in 10 wt% NaCl brine and Saudi medium crude oil.

	Temperature (°C)				
	25	40	50	70	90
BTBAC (5000 ppm)	0.361 ₁	0.275 ₅	0.233 ₀	0.167 ₂	0.065 ₁
BTMAC (5000 ppm)	0.337 ₀	0.258 ₁	0.219 ₁	0.148 ₁	0.056 ₁
MTPPBr (5000 ppm)	0.328 ₁	0.251 ₁	0.221 ₃	0.106 ₁	0.023 ₁

Table 6

IFT values (mN/m) for different salts and hydrogen bond donors in 10 wt% NaCl aqueous solution and Saudi medium oil.

Salt	Conc. (ppm)	Temperature (°C)				
		25	40	50	70	90
MTPPBr	1000	6.240 ₁₀	5.750 ₂₀	5.290 ₁₀	2.290 ₁₀	1.630 ₆₀
	2000	5.510 ₄₀	5.150 ₃₀	4.730 ₂₀	1.330 ₅₀	1.160 ₁₀
	3000	0.319 ₁	0.259 ₂	0.212 ₁	0.106 ₁	0.040 ₁
	5000	0.319 ₂	0.251 ₂	0.210 ₂	0.105 ₃	0.039 ₁
	10,000	0.318 ₂	0.247 ₁	0.209 ₂	0.104 ₁	0.023 ₁
	15,000	0.316 ₁	0.245 ₁	0.206 ₁	0.103 ₄	0.029 ₁
Glycerol	1000	6.770 ₈₀	6.200 ₅₀	5.420 ₇₀	2.340 ₃₀	2.050 ₂₀
	2000	6.580 ₂₀	5.910 ₃₀	4.900 ₅₀	2.060 ₁₀	1.840 ₈₀
	3000	0.418 ₁	0.406 ₁	0.292 ₁	0.229 ₁	0.092 ₉
	5000	0.415 ₁	0.401 ₁	0.291 ₁	0.225 ₁	0.086 ₇
	10,000	0.410 ₅	0.401 ₃	0.286 ₂	0.213 ₁	0.076 ₁
	15,000	0.407 ₃	0.398 ₄	0.283 ₃	0.212 ₁	0.063 ₄
Urea	1000	5.110 ₂₀	4.830 ₇₀	3.560 ₁₀	2.590 ₂₀	2.300 ₁₀
	2000	4.950 ₄₀	4.410 ₁₀	3.030 ₂₀	2.350 ₁₀	2.020 ₃₀
	3000	0.461 ₁	0.397 ₁	0.297 ₂	0.205 ₁	0.121 ₂
	5000	0.465 ₂	0.401 ₁	0.289 ₂	0.193 ₁	0.138 ₁₅
	10,000	0.450 ₁	0.398 ₂	0.281 ₂	0.191 ₆	0.138 ₁
	15,000	0.449 ₁	0.397 ₁	0.279 ₁	0.186 ₂	0.138 ₂
ChCl	1000	6.590 ₂₀	5.880 ₁₀	5.090 ₁₀	2.250 ₆₀	2.050 ₁₀
	2000	5.930 ₄₀	5.430 ₇₀	4.780 ₂₀	2.340 ₁₀	1.890 ₁₀
	3000	0.362 ₁	0.279 ₁	0.240 ₁	0.166 ₁	0.071 ₁
	5000	0.360 ₁	0.277 ₅	0.237 ₂	0.164 ₂	0.069 ₁
	10,000	0.347 ₂	0.260 ₂	0.227 ₁	0.168 ₁	0.046 ₃
	15,000	0.347 ₁	0.254 ₁	0.218 ₁	0.164 ₃	0.030 ₂

Fig. 4 and Table 5. The best result was obtained by using MTPPBr. Once again, it is obvious that IFT values in all cases decreased with increasing temperature. Fig. 4 also displays the IFT comparison of some selected surfactants having same concentration (5000 ppm) at different temperature in 10 wt% NaCl solution. The IFT values decreased with increasing temperature for all surfactants. Overall, the best results were achieved by using DES1, DES2 and MTPPBr.

In order to find the optimal concentration of the salt or the hydrogen bond donor required to obtain the minimum IFT value, we reduced their concentration in the solution and we measured their effect on the IFT value. Table 6 and Fig. 5 show the corresponding results where it is clear that the optimum concentration is about 3000 ppm. Higher concentrations caused negligible decrease in IFT.

It is obvious from the above discussion that the addition of the selected DESs or any of their individual constituents resulted in the decrease of IFT. This contradicts with the results reported by Mohsenzadeh et al. [45] who reported that the used DES increased the IFT between the brine and Omani oil. It should be noted here

Table 7

IFT measurements (mN/m) of neat DES2 and its solutions in 10 wt% NaCl brine and Saudi medium oil.

	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

that the DES concentration used by Mohsenzadeh et al. (50 vol%) was much higher than that used in this work. However, in order to make a fair comparison we measured the IFT of neat DES2 and high concentration of it in brine and Saudi medium oil, Table 7. The results showed that IFT decreases with the addition of the DES for all concentrations. Moreover, the IFT between neat DES2 and Saudi medium oil is very small.

3.1. Molecular study of the water effect on the DES structure

In order to have an economical EOR using DESs, the DESs must be dissolved in brine solution with optimum concentration, 3000 ppm. Since the components of the used DESs were combined by H-bonding, it was very important to explore the effect of water on the interaction forces between the salt and the hydrogen bond donor forming the DES.

The existence of hydrogen bonds in DES was observed in several systems including DES and natural deep eutectic solvents (NADES) by using ¹H NMR and different 2D NMR (NOESY and HOESY) [44,52,53]. In this study, we have investigated the nature of molecular interactions that occur in DES1 (ChCl:glycerol) and how water affect these interactions. The NOESY spectrum revealed the existence of strong interactions between the protons of methyl group of ChCl and both the protons of methylene and the protons of hydroxyl groups (connected to methylene group) from glycerol. These protons also interact with hydroxyl group of ChCl (Fig. 6). These observations suggest that hydrogen bonds were formed between hydroxyl groups of glycerol and chloride ion from ChCl. To study the effect of addition of water on hydrogen bonds formed in ChCl:glycerol DES two dilutions were chosen (25 wt% and 50%). The NOESY analysis of DES diluted with 25 wt% shows strong interactions between water and both ChCl (methyl groups) and glycerol (methylene and its hydroxyl groups), Fig. 7, and a weak interaction between methyl groups from ChCl and hydroxyl groups from glycerol, implying that water formed hydrogen bonds between both ChCl and glycerol but the DES system still exists. This observation was confirmed by HOESY analysis (provided as Supplementary material, Fig. S1) which confirm the interaction between carbon atoms of methylene from glycerol and protons of methylene group connected to hydroxyl group from ChCl. With 50% of dilution of DES, only interactions between water and both ChCl and glycerol were revealed and no interaction between DES itself was observed. This clearly shows that all hydrogen bond interactions in the DES were broken by the addition of water, Fig. 8. These observations were confirmed by ¹H NMR analysis, also provided as Supplementary material (Table S1, and Fig. S2). Indeed, by

adding water, the peaks of all hydrogen atoms contributing in the DES hydrogen bonds showed a different field shift, except hydrogen atoms of the methylene groups because those atoms have no contribution even in the pure DES hydrogen bond interactions. A continuous significant up-field shift of all hydroxyl groups from glycerol (4.49 ppm, 4.62, 4.74 for protons of hydroxyl groups connect to methylene and 4.55 ppm, 4.66, 4.77 for proton of hydroxyl group connect to methyl group) and HDO signal (from 3.83 ppm to 3.99) with water ratio increasing was observed and signal of methyl groups from ChCl was moved to downfield shift. The reason for these modifications of field shifts is that water destroys the hydrogen bonds in ChCl:glycerol DES and forms a new one with chloride choline and glycerol. This phenomenon was also observed in ChCl:glycerol (1:2) and ChCl:urea (1:2) DES mixtures and, recently, in 1,2-propanediol:ChCl:water mixture as NADES by Gutiérrez et al. [52] and Dai et al. [54]. This result show that ChCl:glycerol (1:3) DES conserves its structure despite dilution in DMSO, and while the content of water is below 25% the interactions of components of DES become weak. However, the addition of 50% water breaks the hydrogen bonding between the salt and the hydrogen bond donor so that no interactions between glycerol and ChCl was observed.

4. Conclusion

The effect of the addition of two DESs, choline chloride/urea and choline chloride/glycerol, on the IFT of 10 wt% NaCl brine and Saudi medium oil at different concentrations and temperatures was investigated. It was found that both choline chloride/urea and choline chloride/glycerol DESs reduced the IFT to a large extent. In addition, it was found that the increase of temperature and concentration of the DES decreased the IFT. The effect of the addition of the salt and/or the hydrogen bond donor of the DES, without forming the corresponding DES, on IFT values was also investigated. It was also found that, in most cases, the effect of the addition of the DES or its corresponding constituents on the IFT is the same.

Furthermore, ^1H NMR and different 2D NMR (NOESY and HOESY) were used to investigate the nature of molecular interactions that occur in studied DESs and how water affects these interactions. It was found that while the content of water is below 25 wt% the interactions of components of DES become weak. However, the addition of 50 wt% water breaks the hydrogen bonding between the salt and the hydrogen bond donor so that no interactions were observed.

Acknowledgement

This research was funded by the Deanship of Scientific Research at King Saud University through the International Research Group number IRG14-13.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2015.10.005>.

References

- [1] J. Sheng, *Modern Chemical Enhanced Oil Recovery: Theory and Practice*, Elsevier Science, 2010.
- [2] M. Benzagouta, I. AlNashef, W. Karnanda, K. Al-Khidir, Ionic liquids as novel surfactants for potential use in enhanced oil recovery, *Korean J. Chem. Eng.* 30 (2013) 2108–2117.
- [3] S. Hezave, S. Dorostkar, M. Ayatollahi, Dynamic interfacial tension behavior between heavy crude oil and ionic liquid solution (1-dodecyl-3-methylimidazolium chloride ([C12mim][Cl] + distilled or saline water/heavy crude oil)) as a new surfactant, *J. Mol. Liq.* 187 (2013) 83–89.
- [4] V. Alvarado, E. Manrique, *Enhanced Oil Recovery: Field Planning and Development Strategies*, Elsevier Science, 2010.
- [5] A.R. Kovscek, Emerging challenges and potential futures for thermally enhanced oil recovery, *J. Pet. Sci. Eng.* 98–99 (2012) 130–143.
- [6] N. Gangoli, G. Thodos, Enhanced oil-recovery techniques—state-of-the-art review, *J. Can. Petrol. Technol.* 16 (1977) 13–20.
- [7] J.J. Sheng, Enhanced oil recovery in shale reservoirs by gas injection, *J. Nat. Gas Sci. Eng.* 22 (2015) 252–259.
- [8] F.M. Orr, *Theory of Gas Injection Processes*, Tie-Line Publications, 2007.
- [9] X. Zhou, M. Dong, B. Maini, The dominant mechanism of enhanced heavy oil recovery by chemical flooding in a two-dimensional physical model, *Fuel* 108 (2013) 261–268.
- [10] X. Xie, W.W. Weiss, Z.J. Tong, N.R. Morrow, Improved oil recovery from carbonate reservoirs by chemical stimulation, *SPE J.* 10 (2005) 276–285.
- [11] J. Fink, *Petroleum Engineer's Guide to Oil Field Chemicals and Fluids*, Elsevier Science, 2011.
- [12] Q. Liu, M. Dong, W. Zhou, M. Ayub, Y.P. Zhang, S. Huang, Improved oil recovery by adsorption–desorption in chemical flooding, *J. Pet. Sci. Eng.* 43 (2004) 75–86.
- [13] J. Sheng, *Enhanced Oil Recovery Field Case Studies*, Elsevier Science, 2013.
- [14] M. Algharaib, A. Alajmi, R. Gharbi, Improving polymer flood performance in high salinity reservoirs, *J. Pet. Sci. Eng.* 115 (2014) 17–23.
- [15] K.M. Ko, B.H. Chon, S.B. Jang, H.Y. Jang, Surfactant flooding characteristics of dodecyl alkyl sulfate for enhanced oil recovery, *J. Ind. Eng. Chem.* 20 (2014) 228–233.
- [16] S. Iglauer, Y. Wu, P. Shuler, Y. Tang, W.A. Goddard III, New surfactant classes for enhanced oil recovery and their tertiary oil recovery potential, *J. Pet. Sci. Eng.* 71 (2010) 23–29.
- [17] D.-y. Yin, H. Pu, Numerical simulation study on surfactant flooding for low permeability oilfield in the condition of threshold pressure, *J. Hydrodyn. Ser. B* 20 (2008) 492–498.
- [18] M. Zargartalebi, R. Kharrat, N. Barati, Enhancement of surfactant flooding performance by the use of silica nanoparticles, *Fuel* 143 (2015) 21–27.
- [19] L.L. Schramm, *Surfactants: Fundamentals and Applications in the Petroleum Industry*, Cambridge University Press, 2000.
- [20] F.D.S. Curbelo, V.C. Santanna, E.L.B. Neto, T.V. Dutra Jr, T.N.C. Dantas, A.A.D. Neto, A.I.C. Garnica, Adsorption of nonionic surfactants in sandstones, *Colloids and Surf. A: Physicochem. Eng. Aspects* 293 (2007) 1–4.
- [21] D.O. Shah, R.S. Schechter, A.I.O.C Engineers, *Improved Oil Recovery by Surfactant and Polymer Flooding*, Academic Press, 1977.
- [22] E.M. Kutschmann, G.H. Findenegg, D. Nickel, W. von Rybinski, Interfacial tension of alkylglycosides in different APG/oil/water systems, *Colloid Polym. Sci.* 273 (1995) 565–571.
- [23] M. Kahlweit, R. Strey, G. Busse, Effect of alcohols on the phase behavior of microemulsions, *J. Phys. Chem.* 95 (1991) 5344–5352.
- [24] B. Förster, H. Guckenbiehl, Physico-chemical basics of microemulsions with alkyl polyglycosides, in: H.J. Jacobasch (Ed.), *Interfaces, Surfactants and Colloids in Engineering*, Steinkopff, 1996, pp. 105–112.
- [25] D.W. Green, G.P. Willhite, *Enhanced Oil Recovery*, Henry L. Doherty Memorial Fund of AIME Society of Petroleum Engineers, 1998.
- [26] K. Hill, O. Rhode, Sugar-based surfactants for consumer products and technical applications, *Eur. J. Lipid Sci.* 101 (1999) 25–33.
- [27] Y. Wu, S. Iglauer, P.J. Shuler, Y. Tang, M. Blanco, W.A. Goddard, Synergistic Effect of Alkyl Polyglycoside and Sorbitan Mixtures on Lowering Interfacial Tension and Enhancing Oil Recovery, *Proceedings of the ACS 227th National Meeting, Division of Petroleum Chemistry*, vol. 49, no. 2, pp 208–210, Anaheim, CA, USA, 2004.
- [28] P. Mwangi, An experimental study of surfactant enhanced waterflooding, Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Master of Science in Petroleum Engineering, in: *In: The Craft and Hawkins Department of Petroleum Engineering By Paulina Mwangi BS & BA*, University of Rochester, 2010.
- [29] H. Gong, X. Xin, G. Xu, Y. Wang, The dynamic interfacial tension between HPAM/C17H33COONa mixed solution and crude oil in the presence of sodium halide, *Colloids and Surf. A: Physicochem. Eng. Aspects* 317 (2008) 522–527.
- [30] J. Zhang, G. Li, F. Yang, N. Xu, H. Fan, T. Yuan, L. Chen, Hydrophobically modified sodium humate surfactant: ultra-low interfacial tension at the oil/water interface, *Appl. Surf. Sci.* 259 (2012) 774–779.
- [31] A. Bera, T. Kumar, K. Ojha, A. Mandal, Screening of microemulsion properties for application in enhanced oil recovery, *Fuel* 121 (2014) 198–207.
- [32] Z. Zhao, F. Liu, W. Qiao, Z. Li, L. Cheng, Novel alkyl methylnaphthalene sulfonate surfactants: a good candidate for enhanced oil recovery, *Fuel* 85 (2006) 1815–1820.
- [33] Y. Zhu, G. Xu, H. Gong, D. Wu, Y. Wang, Production of ultra-low interfacial tension between crude oil and mixed brine solution of Triton X-100 and its oligomer Tyloxapol with cetyltrimethylammonium bromide induced by hydrolyzed polyacrylamide, *Colloids and Surf. A: Physicochem. Eng. Aspects* 332 (2009) 90–97.
- [34] S. Sakthivel, S. Velusamy, R.L. Gardas, J.S. Sangwai, Adsorption of aliphatic ionic liquids at low waxy crude oil–water interfaces and the effect of brine, *Colloids and Surf. A: Physicochem. Eng. Aspects* 468 (2015) 62–75.
- [35] A. Zeinolabedini Hezave, S. Dorostkar, S. Ayatollahi, M. Nabipour, B. Hemmateenejad, Effect of different families (imidazolium and pyridinium) of ionic liquids-based surfactants on interfacial tension of water/crude oil system, *Fluid Phase Equilib.* 360 (2013) 139–145.

- [36] X.-l. Wei, X.-h. Wang, J. Liu, D.-z. Sun, B.-l. Yin, X.-j. Wang, Adsorption kinetics of 3-alkoxy-2-hydroxypropyl trimethyl ammonium chloride at oil–water interface, *Appl. Surf. Sci.* 261 (2012) 237–241.
- [37] S. Fu, W. Zhou, Z. Wang, B. Yin, J. Liu, D. Sun, X. Wei, Study on dynamic interfacial tension of 3-dodecyloxy-2-hydroxypropyl trimethyl ammonium bromide at liquid/liquid interface, *Fluid Phase Equilib.* 269 (2008) 93–97.
- [38] J.C. Lim, E.-k. Kang, J.-m. Park, H.C. Kang, B. Min Lee, Syntheses and surface active properties of cationic surfactants having multi ammonium and hydroxyl groups, *J. Ind. Eng. Chem.* 18 (2012) 1406–1411.
- [39] M. Pons-Jiménez, R. Cartas-Rosado, J.M. Martínez-Magadán, R. Oviedo-Roa, R. Cisneros-Dévora, H.I. Beltrán, L.S. Zamudio-Rivera, Theoretical and experimental insights on the true impact of C12TAC cationic surfactant in enhanced oil recovery for heavy oil carbonate reservoirs, *Colloids and Surf. A: Physicochem. Eng. Aspects* 455 (2014) 76–91.
- [40] E. Müller, H.-D. Dörfler, Adsorption and inhibition effects of homologous phosphonium bromides: Part II. Behaviour in ethanol/water electrolyte solutions, *J. Electroanal. Chem. Interfacial Electrochem.* 121 (1981) 169–177.
- [41] E.-k. Kang, B.M. Lee, H.A. Hwang, J.C. Lim, A novel cationic surfactant having two quaternary ammonium ions, *J. Ind. Eng. Chem.* 17 (2011) 845–852.
- [42] I.M. Banat, R.S. Makkar, S. Cameotra, Potential commercial applications of microbial surfactants, *Appl. Microbiol. Biotechnol.* 53 (2000) 495–508.
- [43] A.P. Abbott, D. Boothby, G. Capper, D.L. Davies, R.K. Rasheed, Deep eutectic solvents formed between choline chloride and carboxylic acids: versatile alternatives to ionic liquids, *J. Am. Chem. Soc.* 126 (2004) 9142–9147.
- [44] Y. Dai, J. van Spronsen, G.-J. Witkamp, R. Verpoorte, Y.H. Choi, Natural deep eutectic solvents as new potential media for green technology, *Anal. Chim. Acta* 766 (2013) 61–68.
- [45] A. Mohsenzadeh, Y. Al-Wahaibi, A. Jibril, R. Al-Hajri, S. Shuwa, The novel use of Deep Eutectic Solvents for enhancing heavy oil recovery, *J. Pet. Sci. Eng.* 130 (2015) 6–15.
- [46] M. Albaz, A. Bilgesu, O. Tutkun, The measurement of interfacial tension by drop-weight method, *Commun. Fac. Sci. Univ. Ank. Ser. B* 34 (1988) 103–112.
- [47] Q. Zhang, K. De Oliveira Vigier, S. Royer, F. Jerome, Deep eutectic solvents: syntheses, properties and applications, *Chem. Soc. Rev.* 41 (2012) 7108–7146.
- [48] K. Shahbaz, S. Baroutian, F.S. Mjalli, M.A. Hashim, I.M. AlNashef, Densities of ammonium and phosphonium based deep eutectic solvents: prediction using artificial intelligence and group contribution techniques, *Thermochim. Acta* 527 (2012) 59–66.
- [49] K. Shahbaz, F.S. Mjalli, M.A. Hashim, I.M. AlNashef, Prediction of the surface tension of deep eutectic solvents, *Fluid Phase Equilib.* 319 (2012) 48–54.
- [50] Z. Ye, F. Zhang, L. Han, P. Luo, J. Yang, H. Chen, The effect of temperature on the interfacial tension between crude oil and gemini surfactant solution, *Colloids and Surf. A: Physicochem. Eng. Aspects* 322 (2008) 138–141.
- [51] H. Zhang, M. Dong, S. Zhao, Which one is more important in chemical flooding for enhanced oil recovery, lowering interfacial tension or reducing water mobility? *Energy Fuels* 24 (2010) 1829–1836.
- [52] M.C. Gutiérrez, M.L. Ferrer, C.R. Mateo, F. del Monte, Freeze-drying of aqueous solutions of deep eutectic solvents: a suitable approach to deep eutectic suspensions of self-assembled structures, *Langmuir* 25 (2009) 5509–5515.
- [53] M.C. Gutiérrez, M.L. Ferrer, L. Yuste, F. Rojo, F. del Monte, Bacteria incorporation in deep-eutectic solvents through freeze-drying, *Angew. Chem. Int. Ed.* 49 (2010) 2158–2162.
- [54] Y. Dai, G.-J. Witkamp, R. Verpoorte, Y.H. Choi, Tailoring properties of natural deep eutectic solvents with water to facilitate their applications, *Food Chem.* 187 (2015) 14–19.