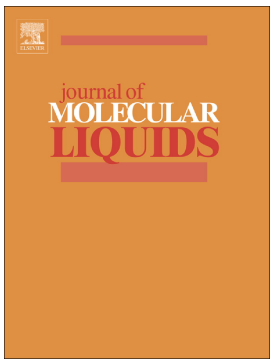

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Synthesis and characterization of eight hydrophilic imidazolium-based ionic liquids and their application on enhanced oil recovery

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Abstract

In order to difficulties in producing large amount of crude oil and remaining oil by primary and secondary oil recovery processes, enhanced oil recovery (EOR) techniques have been developed. Water injection is one of the EOR methods which has shown great potential in recent years. The water flooding process is more effective when the injected water is enriched by chemicals which improves the oil recovery by reducing interfacial tension (IFT) and alternating wettability. In this work eight long alkyl chain imidazolium based ionic liquids (ILs) including Octyl, Decyl, Dodecyl and Tetradecyl methylimidazolium and two different anions namely Chlorid and trihydrogen diphosphate (THDP), were synthesized and characterized by ^{1}HNMR and elemental analysis. As a nobility it should be noted that ILs containing THDP anion have not been synthesized yet and they were used in upstream oil industry for the first time. Furthermore, some physicochemical properties were investigated for studied ILs as a function of temperature. The synthesized ILs were examined as additives in injected water to reduce the IFT in water flooding process. The critical micelle concentration (CMC) point and IFT of enriched sea water by ILs/crude oil, were measured as a function of ILs concentration. The results showed that ILs can be good candidates for EOR technology due to their significant behavior in IFT reduction and their low consumption. The consumed concentrations for ILs were observed at ppm levels, so they are favorable choices when economic concerns are considered. According to obtained results, as the alkyl chain was longer, the CMC point and IFT values were lower. Moreover the investigation of IFT values, revealed that ILs containing THDP anion were more efficient in IFT reduction compared with ILs including chloride anion. [C_{14}mim][Cl] and [C_{14}mim][THDP] were the most effective ILs which 50 and 25 ppm of these ILs, reduced the IFT values to 0.65 ± 0.04 and 0.5 ± 0.02, respectively.

Keywords: Hydrophilic ILs, Synthesis, IFT, CMC point, EOR.

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1. Introduction

In order to reducing easy to access oil, increasing global oil demand and crude oil high price, it is important to extract more oil from the existed oil reservoirs by introducing new technologies [1-3]. Only 20-35% of oil in place can be produced by naturally depletion [4, 5]. Enhanced oil recovery (EOR) methods have been developed to recover large amount of crude oil are trapped in pore structure which cannot be extracted by traditional methods [6-8]. The most commonly used secondary EOR method to improve the productivity of the reservoirs, are composed of two main categories: miscible and immiscible injection [9-11]. Among these technologies, water injection which is part of immiscible injection methods is more effective when one or several chemicals are added to injected water to improve the sweep efficiency and mobilize trapped oil in the reservoirs [12-15]. Interfacial tension (IFT) reduction and wettability alteration to modify the capillary number in the oil reservoirs, are two main mechanism in the enriched water injection by chemicals which causes increase the oil recovery [16, 17].

Some additives in water injection process such as conventional surfactants are unable to tolerate the harsh reservoir conditions such as high salinity and high temperature [18]. Furthermore, due to their high cost, high toxicity, high consumption and many other side effect, ionic liquids (ILs) have used as a type of more cost-effective additives in water injection [8]. Ionic liquids are molten salts which have attracted much attention as potential alternative to traditional organic solvents [19]. Their interesting properties includes high thermal and chemical stability, non-flammability, low vapor pressure, low melting point and high ionic conductivity [20-23].

The application of ILs in the oil industry is very extensive. ILs have been used in refining stage of crude oil, deposition of asphaltenes and parafines in crude oil and manufacturing process of valuable petrochemical products [24]. In terms of molecular structure, ionic liquids exhibit characteristics of cationic surfactants (long carbon chain substituents appended to a charged cationic head group) [25]. Over the past few years, many researchers applied ILs as surfactant in EOR. Benzagouta et al. (2014) [25] introduced a special type of ionic liquid namely Ammoeng which were used for IFT reduction in different salinity and temperature. Bin-Dahbagh et al. (2015) [2] investigated several

ammonium and imidazolium based ILs as surfactant. Zeinolabedini Hezave et al. (2012) [16] studied the effect of different families (imidazolium and pyridinium) of ionic liquids-based surfactants on interfacial tension of water/crude oil system. Lago et al. (2012) [9] used Phosphonium IL as novel surfactant, an alternative to conventional surfactants.

In this work eight hydrophilic imidazolium based ionic liquids were synthesized and characterized by ^{1}HNMR and CHNO elemental analysis. The chemical structures of synthesized are shown in Table 1. ILs containing trihydrogen diphosphate [THDP] anion were synthesized and used in upstream oil industry for the first time. Since the [C_8mim][Cl], [C_{10}mim][Cl], [C_8mim][THDP] and [C_{10}mim][THDP] were liquids, their physicochemical properties such as density, viscosity and refractive index were measured in temperature range 10 to 90 °C and atmospheric pressure. Also the effects of temperature, alkyl chain, and anion type on physicochemical properties were investigated.

Table 1

A comprehensive literature survey showed that the effects of ILs on IFT of formation brine/crude were discussed in previous studies, but in this work the IFT between injected water and crude oil was studied as a known scenario in water injection process.

The synthesized ILs were used to reduce the IFT between oil and injected water. Usually water injection process, is faced with many problems such as formations damage which is caused by the incompatibility between injected water and formation water in reservoir. In general, phosphate containing species such as diphosphoric acid and polyphosphoric acid have been used as anti-scale. Hence in this research, it has been tried to synthesize the task specific ILs that are used as water injection additives and anti-scale. Besides the effects of anion, cation and ILs concentration on IFT reduction were investigated. The CMC point was found for all ILs as a function of efficiency of surface active ILs.

2. Experimental

2.1. Materials

1-methylimidazole, 1-chlorooctane, 1-chlorodecane, 1-chlorododecane and 1-chlorotetradecane were pursued from Merck and were distilled before use. All other starting materials and solvents were used as received without any further treatment. These materials included pyrophosphoric acid (Aldrich, technical grade), diethyl ether (Merck, ≥

99%), silver nitrate (Merck, ≥ 99%), ethanol (Merck, ≥ 96%), potassium hydroxide (Merck, ≥ 99%). High purity of N_2 gas was prepared from Roham Gas Co. (Tehran, Iran). Water used was freshly deionized and distilled before use. Physical properties of Crude oil which was obtained from one of the Iranian oilfield are shown in Table 2. The chemical analysis of sea water is given in Table 3.

Table 2 and 3

2.2. Apparatus and Procedure

The purity of synthesized ILs was proven by ^{1}HNMR (Bruker Avance 500 MHz spectrometer) and elemental analysis CHNO (vario max, elementar, Germany). The interfacial tension between aqueous and oleic phases, IL solution and crude oil respectively, was measured using pendant drop method (KRUSS, SITE-100; KRUSS, Germany). The reported accuracy of the measured IFT is ±0.01 mN/m. Water content was measured by 851 Titrando, coulometric Karl Fischer apparatus supplied by Metrohm (Switzerland). The densities and viscosities of ILs were measured using an automated Anton Paar SVM-3000 digital double-tube visco-densimeter at atmospheric pressure and temperature range 10 to 90°C. The precision in experimental measurements has been found to be better than $\pm 1\times10^{-2}$ g.cm^{-3} for the density and ±1 mPa.s for the viscosity. The calibration was checked periodically with pure liquids (supplied by Cannon Co.) with known density and viscosity at several temperatures.

Refractive indices of synthesized samples were measured by using a refractometer Model J357 supplied by Rudolph Company. The apparatus was calibrated with isopropyl alcohol and water at different temperatures from 10 to 90°C.

2.2.1. IFT measurement

Pendant drop and rising bubble are two mechanism which are considered based on density of balk and drop in IFT measurement of liquid-liquid system. In this research, the density of crude oil was less than sea water density, thus rising bubble mechanism was performed. The IFT measurements were performed inside an optical glass cell filled with sea water enriched with ILs and was placed in a jacket holder at 25±0.1°C. A sufficient drop size of oil was injected upward to the tip of needle as rising bubble which was immersed in the

balk of sea water. The final stabilized drop was imaged and processed by the software for measuring the IFT.

Generally, a pendant drop apparatus consists of three parts: an experimental cell, an illuminating/viewing system and a data acquisition system to calculate the IFT value. In this method, the profile of an oil rising bubble which is suspended in IL solution, is determined at mechanical by the balance between gravity and surface forces. Andreas proposed the following equations to calculate the IFT.

$$\gamma = \frac{g D_e^2 \Delta\rho}{\mathrm{H}} \qquad (2)$$

Where γ is the interfacial tension, Δρ is the density difference between sea water and crude oil, D_e is the equatorial diameter of the drop, H is a correction factor which is related to the shape factor of the pendant drop, S, defined as:

$$S = \frac{D_s}{D_e} \qquad (3)$$

Where D_s is the drop diameter measured horizontally at a distance D_e away from the apex of the drop [26, 27].

2.3. Synthesis of ILs

The synthesis procedure of [C_8mim][Cl], [C_{10}mim][Cl], [C_{12}mim][Cl] and [C_{14}mim][Cl]are given as below:

ILs containing chloride anion were synthesized by reacting 1-methylimidazole (0.1mol) with excess amount of 1-cloroalkane (1-chlorooctane, 1-chlorodecane, 1-chlorododecane or 1-chlorotetradecane) (0.11mol) without any additional solvent. At first the reaction mixture was heated and continually stirred at 80 °C for 72-120 h in a round bottomed flask, fitted with a reflux condenser, under N_2 atmosphere. Then it was cooled to room temperature and washed thrice with 50 ml diethyl ether to remove excess starting material. Finally the resulting products were dried under vacuum at 60 °C for 48 h to remove all solvents [28]. To prove the synthesis verification, ILs were tested with $AgNO_3$ and white AgCl precipitation was seen, so no further purification was required.

Synthesis of ILs containing [C_8mim][THDP], [C_{10}mim][THDP], [C_{12}mim][THDP] and [C_{14}mim][THDP] are given as below

0.1 mol of [$C_n$mim][Cl] (n = 8, 10, 12, 14) and 0.15 mol of KOH were dissolve in 30 and 45 ml ethanol respectively. Then KOH solution was added dropwise to the [$C_n$mim][Cl] solution in a round bottomed flask equipped by magnet stirrer, and KCl white precipitate was immediately observed. The resulting mixture was stirred for another 5 min to ensure that the reaction was complete. [$C_n$mim][OH] solution in ethanol was obtained by filtering the reaction mixture to remove all KCl participation [29]. 0.25 mol pyrophosphoric acid per mol KOH was dissolved in water and added to [$C_n$mim][OH] solution. All the active protons of $H_4P_2O_7$ were neutralized to generate [$C_n$mim]$_4P_2O_7$ and $K_4P_2O_7$. Then, another 0.75 mol $H_4P_2O_7$ per mol of [$C_n$mim][OH] was added in three steps to obtain [$C_n$mim][THDP]. Finally the mixture was placed in a rotary evaporator to remove all solvents and then was dried in a vacuum oven.

2.4. Characterization of synthesized ILs

The synthesized ILs were characterized by ^{1}HNMR and CHNO elemental analysis, to prove the absence of impurities. The elemental analysis and impurity contents of studied ILs are reported in Table 4 and 5.

Table 4 and 5

[C_8mim][Cl]: ^{1}HNMR (500 MHz, D_2O): δH= 8.61 (1H, s), 7.36 (1H, s), 7.32 (1H, s), 4.05 (2H, t), 3.77 (3H, s), 1.72 (2H, quintet), 1.24-1.1 (10H, m), 0.84 (3H, t).

[C_{10}mim][Cl]: ^{1}HNMR (500 MHz, D_2O): δH= 9.29 (1H, s), 7.76 (1H, s), 7.72 (1H, s), 4.15 (2H, t), 3.8 (3H, s), 1.72 (2H, quintet), 1.23-1.15 (14H, m), 0.82 (3H, t).

[C_{12}mim][Cl]: ^{1}HNMR (500 MHz, D2O): δH= 9.12 (1H, s), 7.85 (1H, s), 7.77 (1H, s), 4.1 (2H, t), 3.83 (3H, s), 1.78 (2H, quintet), 1.30-1.21 (18H, m), 0.86 (3H, t).

[C_{14}mim][Cl]: ^{1}HNMR (500 MHz, D2O): δH= 8.97 (1H, s), 7.79 (1H, s), 7.75 (1H, s), 4.17 (2H, t), 3.65 (3H, s), 1.83 (2H, quintet), 1.34-1.2 (22H, m), 0.79 (3H, t).

[C_8mim][$H_3P_2O_7$]: ^{1}HNMR (500 MHz, D2O): δH= 9.04 (1H, s), 7.78 (1H, s), 7.82 (1H, s), 4.12 (2H, t), 3.88 (3H, s), 1.70 (2H, quintet), 1.16-1.1 (10H, m), 0.79 (3H, s).

[C_{10}mim][$H_3P_2O_7$]: ^{1}HNMR (500 MHz, D2O): δH= 9.48 (1H, s), 7.91 (1H, s), 7.85 (1H, s), 4.33 (2H, t), 3.89 (3H, s), 1.75 (2H, quintet), 1.27-1.09 (14H, m), 0.82 (3H, t).

[C_{12}mim][$H_3P_2O_7$]: ^{1}HNMR (500 MHz, D2O): δH= 9.21 (1H, s), 7.63 (1H, s), 7.69 (1H, s), 4.21 (2H, t), 3.73 (3H, s), 1.82 (2H, quintet), 1.28-1.13 (18H, m), 0.89 (3H, t).

[C_{14}mim][$H_3P_2O_7$]: ^{1}HNMR (500 MHz, D2O): δH= 8.89 (1H, s), 7.85 (1H, s), 7.77 (1H, s), 4.12 (2H, t), 3.71 (3H, s), 1.88 (2H, quintet), 1.32-1.15 (22H, m), 0.85 (3H, t).

3. Result and discussion

3.1. Physicochemical properties of ILs

The physicochemical properties of [C_8mim][Cl], [C_{10}mim][Cl], [C_8mim][THDP] and [C_8mim][THDP] are given in Table 6, over a wide temperature range of 10 to 90 °C. The density (ρ) and refractive index (n_D) were fitted by least squares using the polynomial of second order expression given by equation (4).

$$Z = A_o + A_1 \times T + A_2 \times T^2 \quad (4)$$

The viscosity values can be represented using the following Ln type equation (5):

$$\ln \eta \text{ (mPa s)} = A_o/T - A_1 \quad (5)$$

Where z is ρ (g.cm^{-3}) and n_D, T is the temperature (°C) and A_o, A_1 and A_2 are the adjustable parameters [30].

The best fit parameters for density, viscosity and refractive index are listed in Table 7.

Table 6 and 7

3.2. Density and viscosity

The effects of temperature, cation and anion type on the density and viscosity of synthesized ILs are shown in Table 6 and Figures 1 and 2. As expected, the measured densities and viscosities were decreased as a function of temperature. According to Fig. 1, the density of ILs was decrease with increasing the alkyl chain length at each temperature. The data clearly indicated that the density was increased in order [C_8mim][THDP] > [C_{10}mim][DHP] > [C_8mim][Cl] > [C_{10}mim][Cl]. The higher density values for [C_8mim][THDP] and [C_{10}mim][THDP] was due to presence of more hetero atoms in comparison with other anions. In general, the density of ILs was increased when anion molecular weight was increased [31]. As shown in Fig. 2, the investigation on viscosity values of ILs exhibited that as the alkyl chain was increased from C_8 to C_{10}, the viscosity was increased which was caused by increasing the van der Waals interaction between the aliphatic alkyl chains [32, 33]. The main reason for high viscosity of [C_8mim][THDP] and [C_{10}mim][THDP] is presence of hydrogen bonding in anions structure and also high molecular weight of these anions compared with ILs containing chloride anion.

Fig. 1 and 2

3.3. Refractive Index

The refractive index is a key parameter to determine the purity and electronic polarizability of ILs. The temperature dependence of refractive indices for synthesized ILs are presented in Table 6 and Fig. 3. The n_D values for the synthesized ILs were decreases in a linear manner with increasing temperature. Figure 4 showed the effects of temperature, anion and cation type of ILs on the refractive indices values. The results showed that the shorter alkyl chain length led to the higher refractive index. It can be explained that, ILs with longer alkyl chain, cannot be close packed in microscopic structure [34]. Increasing trend of refractive index for studied ILs, was as follows: [C_8mim][Cl] > [C_{10}mim][Cl] > [C_8mim][THDP] > [C_{10}mim][THDP]. For synthesized ILs, the refractive indices values were higher than the range of most organic materials.

Fig. 3

3.4. Surface activity of ILs

The critical micelle concentration (CMC) is an important characteristic of a surfactant. At this concentration, surfactant molecules which were placed at surface of solution, associate to form micelles and any further addition of surfactant arrange as micelles, as a result the IFT is not reduced anymore as the surfactant concentration was increased. The CMC point determines surfactant efficiency as the CMC is lower, the surfactant have better efficiency. A lower CMC indicates that less concentration of surfactant is require to obtain the minimum IFT value [6, 25 and 35]. In order to find the CMC of investigated ILs, several experimental IFT tests were performed at different concentrations of ILs in sea water. The salinity was considered constant concentration in this work, because the effect of salinity on TFT have been done in pervious works [6, 16]. However the harsh salinity condition was applied to evaluate the stability of ILs in sea water salinity. All synthesized ILs were stable and efficient in harsh salinity of sea water. The CMC values are listed in Table 8.

Table 8

Table 8 revealed that as the alkyl chain was longer, the CMC value was lower. In order to low CMC value for many synthesized ILs, they can be good candidate when economical concern is a main factor.

3.5. Effect of ILs concentration on IFT between sea water and crude oil

The imidazolium based synthesized ILs in this research were composed of four different alkyl chain length (Octyl, Decyl, Dodecyl and Tetradecyl) and two anion (chloride and trihydrogen phosphate). The IFT of sea water which was enriched by ILs and crude oil was measured at several concentration. Besides the effects of cation and anion type and concentration of ILs were investigated on IFT reduction. According to obtained results listed in Table 9, all eight ILs showed very interesting behavior in IFT reduction. As a result, it can be concluded that the synthesized ILs were able to tolerate the harsh conditions of sea water concentration and they were favorable choices for EOR process, due to IFT reduction.

Table 9

Commonly, long alkyl chain ILs, like surfactant, are consisted of hydrophilic imidazolium head group and hydrophobic alkyl chain tail in cation part. The hydrophobic part extend into the oily phase and the hydrophilic part likes to stay in water phase. As the alkyl chain is longer, the capability of the ILs to reduce the IFT is increased which could be due to the effect of hydrophobic long alkyl chain tail [35]. As clearly can be found in Table 8 and 9, the CMC point and IFT values is decreased as the alkyl chain length is increased.

According to obtained results from Figures 4, 5 and Table 9, as the ILs concentration were increased from 100 to 3000 ppm for [$C_n$mim][x], (n: 8, 10, 12 and x:Cloride and THDP), the IFT of sea water/crude oil were deceased. Due to very low IFT values for [C_{14}mim][Cl] and [C_{14}mim][THDP], ILs concentration was increased from 10 ppm and the IFT was decreased to very low values as shown in Table 9.

Fig. 4 and 5

Furthermore, a detailed investigation in Table 9 and Fig. 4, 5, revealed that a sharp reduction in the IFT was observed when the IL concentration was changed before and after the CMC point of corresponding IL. Comparing the IFT values of ILs containing chloride anion and those who were included THDP anion, it can be concluded that the anion types of ionic liquids is affected on IFT of sea water/ crude oil system. There were a few reports concerning the effects of the anion on IFT between sea water and crude oil. The results demonstrated that the efficiency of ILs containing THDP anion in IFT reduction, was better than ILs with chloride anion. The investigation revealed that the system containing ILs with bigger size and higher viscosity of anion, exhibited higher IFT reduction.

Commonly increasing the viscosity of injected fluid is improved the sweep efficiency, so ILs which have higher viscosity, is more effective to reduce IFT [36].

Conclusion

The eight hydrophilic imidazolium based ionic liquids were synthesized and characterized by ^{1}HNMR and CHNO elemental analysis. ILs including [C_8mim][Cl], [C_{10}mim][Cl], [C_{12}mim][Cl], [C_{14}mim][Cl], [C_8mim][THDP], [C_{10}mim][THDP], [C_{12}mim][THDP] and [C_{14}mim][THDP] were used as surfactants to reduce the IFT between enriched sea water by ILs and crude oil in water injection. As a nobility it should be noted that the effect of synthesized ILs on water injection process as known scenario in secondary EOR, has been proposed for the first time. Moreover, as another nobility ILs containing THDP anion, have not been synthesized yet. The physicochemical properties such as density, viscosity and refractive index were measured for [C_8mim][Cl], [C_{10}mim][Cl], [C_8mim][THDP] and [C_{10}mim][THDP] at temperature range of 10 to 90 °C. According to the obtained results unlike viscosity, other properties such as density and refractive index were decreased while alkyl chain length was increased.

The CMC point as a function of optimized economical and efficient concentration for all ILs was determined and the IFT as a function of sweep efficiency (capillary number) in water injection process, was measured at different ILs concentration by pendant drop method. The results revealed the high efficiency of synthesized ILs in IFT reduction of sea water/crude oil. The used sea water salinity was about 43000 ppm. According to the obtained results, as the alkyl chain length was increased, the CMC point and IFT values were decreased, it means that less IL is required to obtain the minimum IFT, so these ILs are favorable choices in economic circumstances. The best IFT values (0.65 ± 0.04 and 0.5 ± 0.02 mN.m^{-1}) were obtained by [C_{14}mim][Cl] and [C_{14}mim][THDP] while, only 50 and 25 ppm of these ILs was added to sea water. Furthermore the experimental IFT data showed that ILs including THDP anion had the better performance as surfactant to reducing the IFT which is related to the higher viscosity of these ILs compared with ILs having chloride anion.

References

[1] A. Mandal, A. Samanta, A. Bera, K. Ojha, Ind. Eng. Chem. Res. 49 (2010) 12756–12761.

[2] M. S. Bin-Dahbag, A. A. AlQuraishi, M. S. Benzagouta, J. Petrol. Explor. Prod. Technol. 5 (2015) 353-361.

[3] S. Lago, M. Francisco, A. Arce, A. Soto, Energy Fuels. 27 (2013) 5806−5810.

[4] D. Nguyen, N. Sadeghi, C. Houston, Energy Fuels. 26 (2012) 2742−2750.

[5] E. Joonaki, S. Ghanaatian, G Zargar, Iranian Journal of Oil & Gas Science and Technology. 1 (2012) 37-42.

[6] A. Z. Hezave S. Dorostkar, S. Ayatollahi, M. Nabipour, B. Hemmateenejad, J. Mol. Liq. 187 (2013) 83-89.

[7] S. Sakthivel, R. L. Gardas, J. S. Sangwai, Energy Fuels. 30 (2016) 2514–2523.

[8] M. S. Bin-Dahbag, A. A. Al-Quraishi, M. S. Benzagouta, M. M. Kinawy, I. M. Al-Nashef, E. Al-Mushaegeh, J. Pet. Environ. Biotechnol. 4 (2014) 165-171.

[9] S. Lago, H. Rodrı´guez, M. K. Khoshkbarchi, A. Soto, RSC Adv. 2 (2012) 9392–9397.

[10] S. Sakthivel, S. Velusamy, V. C. Nair, T. Sharma, J. S. Sangwai, Fuel. 191 (2017) 239–250.

[11] E. A. Chukwudeme, A. A. Hamouda, Energies, 2 (2009) 714-737.

[12] D. Xie, J. Hou, A. Doda, J. Trivedi, Energy Fuels. 30 (2016) 4583−4595.

[13] H. Zhang, G. Chen, M. Dong, S. Zhao, Z. Liang, Energy Fuels. 30 (2016) 3860−3869.

[14] M. Riahinezhada, L. Romero-Zerónb, N. McManusa, A. Penlidis, Fuel. 203 (2017) 269–278.

[15] P. K. Bikkina, R. Uppaluri, M. K. Purkait, J. Pet. Sci. Technol. 31 (2013) 755–762.

[16] A. Z. Hezave, S. Dorostkar, S. Ayatollahi, M. Nabipour, B. Hemmateenejad, Fluid Phase Equilib 360 (2013) 139– 145.

[17] M. Abdi, S. Moradi, B. Habibniya, S. Kord, Int. J Sci. Emerging Tech. 7 (2014) 302-308.

[18] n. Chegenizadeh, A. Saeedi, X. Quan, .petlm. 11 (2016) 197-211.

[19] R. D. Rogers and G. A. Voth, Acc. Chem. Res. 40 (2007) 1077-1078.

[20] E. M. Siedlecka, M. Czerwicka, S. Stolte, and P. Stepnowski, Curr. Org. Chem. 15 (2011) 1974-1991.

[21] J. Hekayati, A. Roosta and J. Javanmardi, J. Mol. Liq. 225 (2017) 118-126.

[22] P. M. Dean, J. M. Pringle and D. R. MacFarlane, Phys. Chem. Chem. Phys. 12 (2010), 9144-9153.

[23] O. Zech, A. Stoppa, R. Buchner, and W. Kunz, J. Chem. Eng. Data. 55 (2010) 1774-1778.

[24] M. H. Jose-Alberto and A. Jorge, Current Knowledge and Potential Applications of Ionic Liquids in the Petroleum Industry, in Ionic Liquids: Applications and Perspectives, A. Kokorin, Ed., ed Rijeka, InTech publications, Croatia (2011).

[25] M. S. Benzagouta, I. M. AlNashef, W. Karnanda and K. A. Khidir, Korean J. Chem. Eng., 11 (2013) 2108-2117.

[26] E. Y. Arashiro, N. R. Demarquette, Materials Research. 2 (1999) 23-32.

[27] Y. Kitazumi, T. Kakiuch, Langmuir. 25 (2009) 8062–8068.

[28] P. Wasserscheid and T. Welton, in Ionic Liquids in Synthesis 2nd Edition, Willey publications, New York, (2007).

[29] J. Gao, J. Liu, B. Li, W. Liu, Y. Xie, Y. Xin, Y. Yin, X. Jie, J. Gu and Z. Zou, New J. Chem. 35 (2011) 1661-1666.

[30] M. Shamsipur, A. A. Miran Beigi, M. Teymori, S. M. Pourmortazavi and M. Irandoust, J. Mol. Liq. 157 (2010) 43-50.

[31] K. R .Seddon, A. Stark and M. Jose Torr, ACS Symp. Ser. 819 (2002) 34-39.

[32] H. Tokuda, K. Hayamizu, K. Ishii, M. A. B. H. Susan and M. Watanabe, J. Phys. Chem. B, 109 (2005) 6103-6110.

[33] M. Moosavi, F. Khashei, A. Sharifi and M. Mirzaei, Ind. Eng. Chem. Res, 55 (2016) 9087-9099.

[34] X. J. Yan, S. N. Li, Q. G. Zhai, Y. C. Jiang and M. C. Hu, J. Chem. Eng. Data, 59 (2014) 1411-1422.

[35] A. Z. Hezave S. Dorostkar, S. Ayatollahi, M. Nabipour, B. Hemmateenejad, J. Disper. Sci. Technol. 35 (2014) 1483–1491.

[36] A. Bera, H. Belhaj, J. Mol. Liq. 224 (2016) 177-188.

Table. 1. Chemical structures of the synthesized ionic liquids

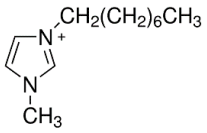
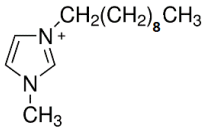
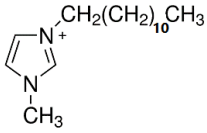
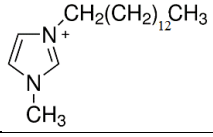
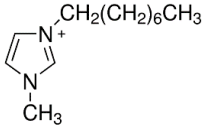
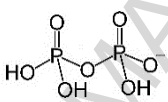
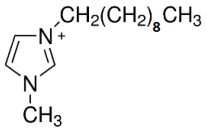
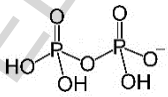
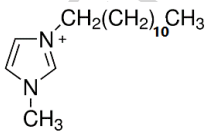
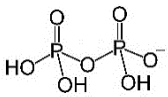
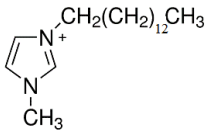
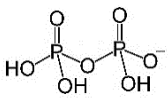
Ionic Liquid	Cation part	Anion part	Abbreviation	Formula	M.W (g/mol)	Purity (%)
1-Octyl-3-methylimidazolium chloride		Cl^-	[C_8mim][Cl]	$C_{12}H_{23}ClN_2$	230.78	99
1-Decyl-3-methylimidazolium chloride		Cl^-	[C_{10}mim][Cl]	$C_{14}H_{27}ClN_2$	258.2	99
1-Dodecyl-3-methylimidazolium chloride		Cl^-	[C_{12}mim][Cl]	$C_{16}H_{31}ClN_2$	286.88	99
1-Tetradecyl-3-methylimidazolium chloride		Cl^-	[C_{14}mim][Cl]	$C_{18}H_{35}ClN_2$	314.94	99
1-Octyl-3-methylimidazolium threehydrogen diphosphate			[C_8mim][THDP]	$C_{12}H_{26}N_2O_7P_2$	372.29	98
1- Decyl-3-methylimidazolium threehydrogen diphosphate			[C_{10}mim][THDP]	$C_{14}H_{30}N_2O_7P_2$	400.34	98
1- Dodecyl-3-methylimidazolium threehydrogen diphosphate			[C_{12}mim][THDP]	$C_{16}H_{34}N_2O_7P_2$	428.40	98
1-Tetradecyl-3-methylimidazolium threehydrogen diphosphate			[C_{14}mim][THDP]	$C_{18}H_{38}N_2O_7P_2$	456.45	98

Table 2. Physical properties of used crude oil

Property	**Crude Oil**
Density of Residual Oil (ambient condition)(g/lit)	0.9135
Molecular Weight of Stock Tank Oil (g/mol)	298
Viscosity (ambient condition) (cP)	4.2325
API Gravity of Residual Oil (°API)	23.25

Table 3. Chemical analysis of sea water.

Component	Composition / ppm
Calcium	500
Magnesium	1642
Sodium	12650
Potassium	460
Lithium	0.1
Barium	0.6
Strontium	4.7
Fe	<0.05
Chloride	23042
Carbonate	4
Bicarbonate	92
Sulfate	3070
Sulfide	2
Total dissolved solids (TDS)	43788

Table 4. The CHNO elemental analysis for synthesized ILs

IL	Chemical Formula	MW (g/mol)	% C		% H		% N		% O	
			cal	exp	cal	exp	cal	exp	cal	exp
C_8mim cl	$C_{12}H_{23}ClN_2$	230.78	62.45	62.33	10.04	10.11	12.14	11.98	-	-
C_{10}mim cl	$C_{14}H_{27}ClN_2$	258.2	64.96	64.8	10.51	10.7	10.82	10.72	-	-
C_{12}mim cl	$C_{16}H_{31}ClN_2$	286.88	66.98	67.06	10.89	10.77	9.76	9.82	-	-
C_{14}mim cl	$C_{18}H_{35}ClN_2$	314.94	68.65	69.01	11.2	11.06	8.89	8.77	-	-
C_8mim THDP	$C_{12}H_{26}N_2O_7P_2$	372.29	38.71	38.56	7.04	6.88	7.52	7.74	30.08	29.89
C_{10}mim THDP	$C_{14}H_{30}N_2O_7P_2$	400.34	42.00	41.92	7.55	7.61	6.99	7.07	27.97	28.01
C_{12}mim THDP	$C_{16}H_{34}N_2O_7P_2$	428.40	44.86	45.04	7.99	8.11	6.54	6.42	26.14	26.07
C_{14}mim THDP	$C_{18}H_{38}N_2O_7P_2$	456.45	47.36	47.8	8.39	7.96	6.14	6.28	24.54	24.73

Table 5. Impurities of the synthesized ionic liquids.

Species	$[C_8mim][Cl]$	$[C_{10}mim][Cl]$	$[C_{12}mim][Cl]$	$[C_{14}mim][Cl]$	$[C_8mim][THDP]$	$[C_{10}mim][THDP]$	$[C_{12}mim][THDP]$	$[C_{14}mim][THDP]$
	Results							
Water content [a], ppm	640	480	340	310	420	510	280	350
Chloride [b], ppm	152914	137183	123628	108963	<10	<10	<10	<10
Bromide [b], ppm	<10	<10	<10	<10	<10	<10	<10	<10
Sulfate [c], ppm	<5	<5	<5	<5	<5	<5	<5	<5
Heavy metals [c] (as Pb), ppm	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Ash content [d], mass%	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Test methods are a) Karl Fischer, b) potentiometry, c) turbidimetry, d) Electric furnace and gravimetry								

The uncertainty in temperature and pressure were ±0.01 ºC and ±0.01 bar respectively.

Table 6. Density (ρ), viscosity (η) and refractive index (n_D) of synthesized ILs

T/°C	ρ/(g.cm^{-3})	η/(mPa.s)	n_D
[C_8mim][Cl]			
10	1.0189 ± 0.0174	-	1.51162 ± 0.0018
20	1.0137 ± 0.0117	34100 ± 1770	1.51011 ± 0.0026
25	1.0119 ± 0.0183	20900 ± 1049	1.50867 ± 0.0030
30	1.0081 ± 0.014	11040 ± 2016	1.50721 ± 0.001
40	1.0022 ± 0.0088	4130 ± 333	1.5043 ± 0.0024
50	0.9970 ± 0.0077	1980 ± 329	1.50152 ± 0.0016
60	0.9903 ± 0.0123	940 ± 149	1.49871 ± 0.0022
70	0.9852 ± 0.0148	338 ± 78	1.49587 ± 0.0031
80	0.9791 ± 0.0108	137 ± 34	1.49343 ± 0.0033
90	0.9736 ± 0.0109	56 ± 15	1.49079 ± 0.0041
[C_{10}mim][Cl]			
10	-	-	-
20	-	-	1.50018 ± 0.0054
25	0.9834 ± 0.0094	-	1.4988 ± 0.0026
30	0.9788 ± 0.0042	-	1.4971± 0.002
40	0.9739 ± 0.0064	5721 ± 370	1.49362 ± 0.0058
50	0.968 ± 0.0029	2648 ± 304	1.48962 ± 0.008
60	0.9619 ± 0.0062	1292 ± 183	1.48646 ± 0.008
70	0.9558 ± 0.0086	489.3 ± 91	1.48334 ± 0.0053
80	0.9501 ± 0.0103	248.15 ± 58	1.48059 ± 0.0063
90	0.9433 ± 0.0091	152.46 ± 64	1.47869 ± 0.0027
[C_8mim][THDP]			
10	-	-	1.47193 ± 0.0053
20	-	-	1.4707 ± 0.0049
25	1.4255 ± 0.0121	23469 ± 1783	1.46949 ± 0.0072
30	1.4219 ± 0.0143	14620 ± 1288	1.46851 ± 0.0054
40	1.4163 ± 0.018	7114 ± 676	1.46654 ± 0.005
50	1.4090 ± 0.0109	2983 ± 594	1.46466 ± 0.0087
60	1.4030 ± 0.0066	1313 ± 329	1.46264 ± 0.0092
70	1.3946 ± 0.0038	683 ± 237	1.46073 ± 0.0048
80	1.3895 ± 0.0112	369.45 ± 79	1.4588 ± 0.004
90	1.3812 ± 0.0101	210.35 ± 56	1.45692 ± 0.007
[C_{10}mim][THDP]			
10	-	-	
20	-	-	
25	-	-	
30	-	-	
40	1.3587 ± 0.0135	8048 ± 556	1.44929 ± 0.0040
50	1.3536 ± 0.0133	3521 ± 680	1.44718 ± 0.0063
60	1.3483 ± 0.0096	1802 ± 318	1.44497 ± 0.0032
70	1.3438 ± 0.0105	893.2 ± 173	1.44308 ± 0.0071
80	1.3384 ± 0.0022	421 ± 54	1.44123 ± 0.0042
90	1.3336 ± 0.0066	253.1 ± 31	1.43902 ± 0.0067

The uncertainty in temperature and pressure were ±0.01 ºC and ±0.01 bar respectively.

Table 7. Fitting parameters of Eqs. (1), (2) used for correlation of the physical properties of ILs studied.

Physical property	A_0	A_1	A_2	R^2
[C_8mim][Cl]				
ρ/(g.cm^{-3})	1.0249	-0.0006	-2×10^{-7}	0.9992
n_D	1.5148	-0.0003	-2×10^{-7}	0.9980
η/(mPa.s)	-21.999	9521.8	-	0.9963
[C_{10}mim][Cl]				
ρ/(g.cm^{-3})	0.9971	-0.0006	-3×10^{-7}	0.9988
n_D	1.509	-0.0004	1×10^{-6}	0.9984
η/(mPa.s)	-18.536	8524.7	-	0.9956
[C_8mim][THDP]				
ρ/(g.cm^{-3})	1.4406	-0.0006	-8×10^{-7}	0.9985
n_D	1.474	-0.0002	-1×10^{-7}	0.9991
η/(mPa.s)	-16.563	7937	-	0.9991
[C_{10}mim][THDP]				
ρ/(g.cm^{-3})	1.3795	-0.0005	2×10^{-7}	0.9997
n_D	1.458	-0.0002	2×10^{-7}	0.9975
η/(mPa.s)	-16.334	7927.9	-	0.9993

Table 8. The obtained CMC point of synthesized ILs

IL	CMC point (ppm)	IFT ($mN.m^{-1}$)
[C_8mim][Cl]	500	1.9 ± 0.39
[C_{10}mim][Cl]	350	1.67 ± 0.23
[C_{12}mim][Cl]	150	1.43 ± 0.15
[C_{14}mim][Cl]	50	0.65 ± 0.04
[C_8mim][THDP]	350	1.52 ± 0.19
[C_{10}mim][THDP]	250	1.21 ± 0.03
[C_{12}mim][THDP]	100	1.1 ± 0.09
[C_{14}mim][THDP]	25	0.5 ± 0.02

Table 9. Effect of synthesized ILs on IFT of crude oil/enriched sea water

[IL] (ppm)	IFT ($mN.m^{-1}$) ± a							
	[C_8mim] [Cl]	[C_{10}mim][Cl]	[C_{12}mim][Cl]	[C_{14}mim] [Cl]	[C_8mim] [THDP]	[C_{10}mim] [THDP]	[C_{12}mim] [THDP]	[C_{14}mim] [THDP]
0	11.66 ± 0.71	11.78 ± 0.69	12.03 ± 0.65	11.97 ± 0.67	11.58 ± 0.72	11.62 ± 0.65	12.11 ± 0.58	11.82 ± 0.61
10	-	-	-	3.49 ± 0.23	-	-	-	4.82 ± 0.21
25	-	-	-	2.85 ± 0.37	-	-	-	0.5 ± 0.02
50	-	-	-	0.65 ± 0.04	-	-	3.89 ± 0.09	0.33 ± 0.06
75	-	-	-	-	-	-	2.43 ± 0.09	0.31 ± 0.09
100	8.23 ± 0.62	6.46 ± 0.71	5.23 ± 0.16	0.5 ± 0.08	7.12 ± 0.43	5.21 ± 0.36	1.1 ± 0.09	0.26 ± 0.08
150	-	-	1.43 ± 0.15	-	-	-	-	-
200	-	4.83 ± 0.43	-	-	-	-	-	-
250	5.23 ± 0.53	3.92 ± 0.61	1.22 ± 0.09	0.53 ± 0.04	3.62 ± 0.62	1.21 ± 0.19	0.96 ± 0.13	0.27 ± 0.05
350	3.56 ± 0.46	1.67 ± 0.23	-	-	1.52 ± 0.26	1 ± 0.08	-	-
500	1.9 ± 0.39	1.35 ± 0.1	0.98 ± 0.1	0.52 ± 0.07	1.35 ± 0.13	0.95 ± 0.11	0.81 ± 0.09	0.2 ± 0.09
750	1.63 ± 0.28	1.16 ± 0.09	0.82 ± 0.07	-	1.39 ± 0.1	0.95 ± 0.09	-	-
1000	1.59 ± 0.35	1.08 ± 0.12	0.78 ± 0.09	0.5 ± 0.03	1.3 ± 0.09	0.87 ± 0.13	0.78 ± 0.09	0.2 ± 0.08
1500	-	1.04 ± 0.14	0.82 ± 0.06	-	1.22 ± 0.1	0.82 ± 0.06	0.62 ± 0.1	-
2000	1.52 ± 0.23	1.08 ± 0.09	0.86 ± 0.1	-	1.2 ± 0.08	0.9 ± 0.09	0.61 ± 0.03	-
3000	1.5 ± 0.18	1.04 ± 0.12	0.85 ± 0.09	-	1.23 ± 0.13	0.83 ± 0.14	0.43 ± 0.07	-

□a is standard deviation obtained using minimum three dependent measurements for each data point.

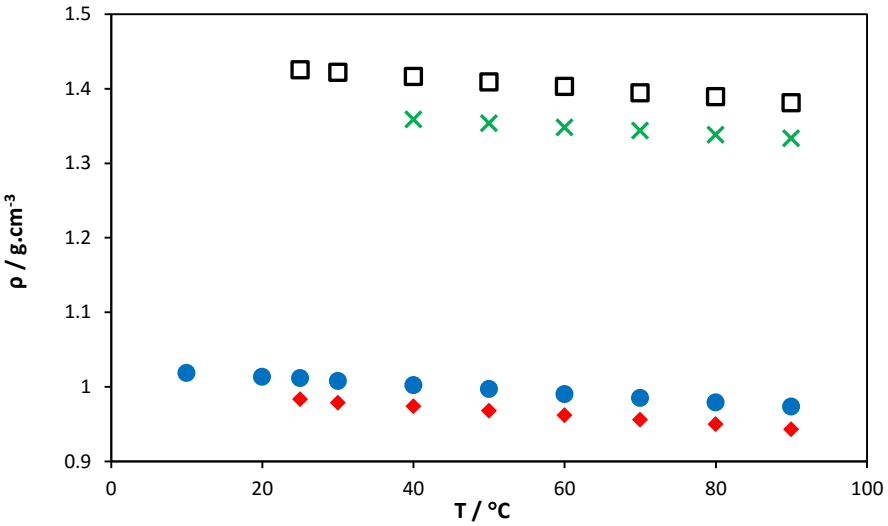


Fig. 1. Experimental values of density, ρ (g/cm^3) against temperature (°C) for (●) ([C_8mim][Cl]), (♦) ([C_{10}mim][Cl]), (□) ([C_8mim][THDP]) and (×) ([C_{10}mim][THDP])

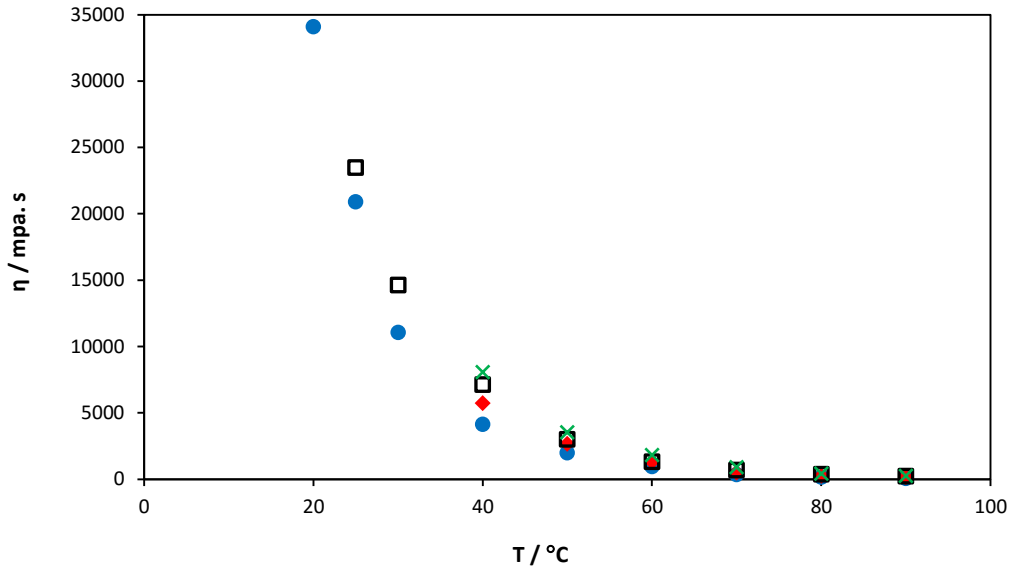


Fig. 2. Experimental values of viscosity η (mpa.s) against temperature (°C) for (●) ([C_8mim][Cl]), (♦) ([C_{10}mim][Cl]), (□) ([C_8mim][THDP]) and (×) ([C_{10}mim][THDP])

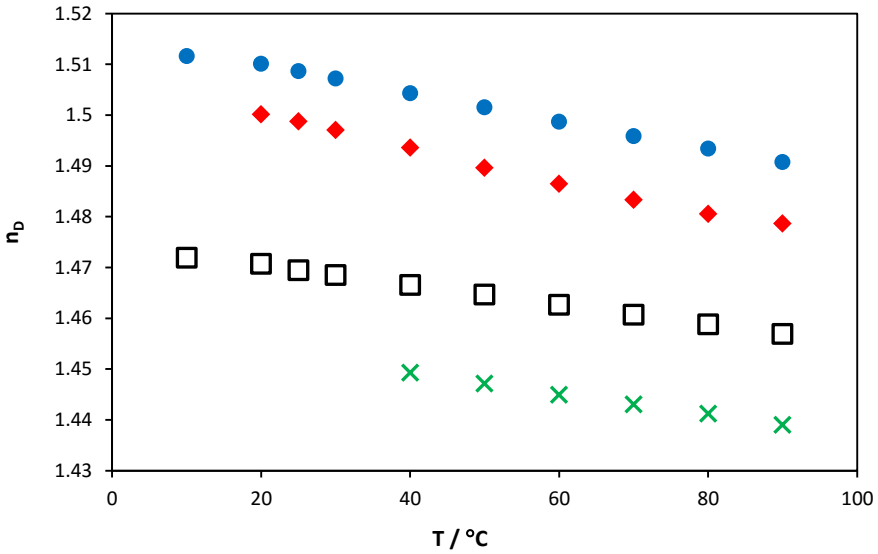


Fig. 3. Experimental values of refractive index n_D, against temperature (°C) for (●) ([C_8mim][Cl]), (♦) ([C_{10}mim][Cl]), (□) ([C_8mim][THDP]) and (×) ([C_{10}mim][THDP])

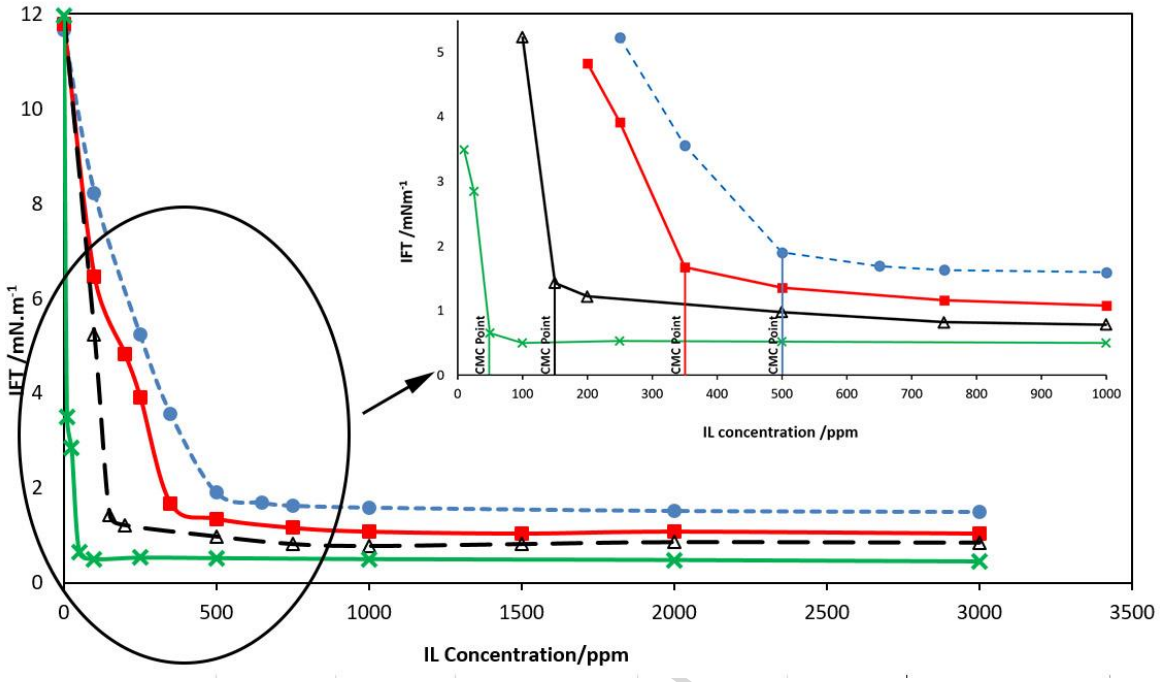


Fig. 4. Effect of ILs (containing chloride anion) concentration on the IFT of sea water and crude oil, (●) [C_8mim][Cl], (■)[C_{10}mim][Cl], (Δ) [C_{12}mim][Cl] and (×) [C_{14}mim][Cl]

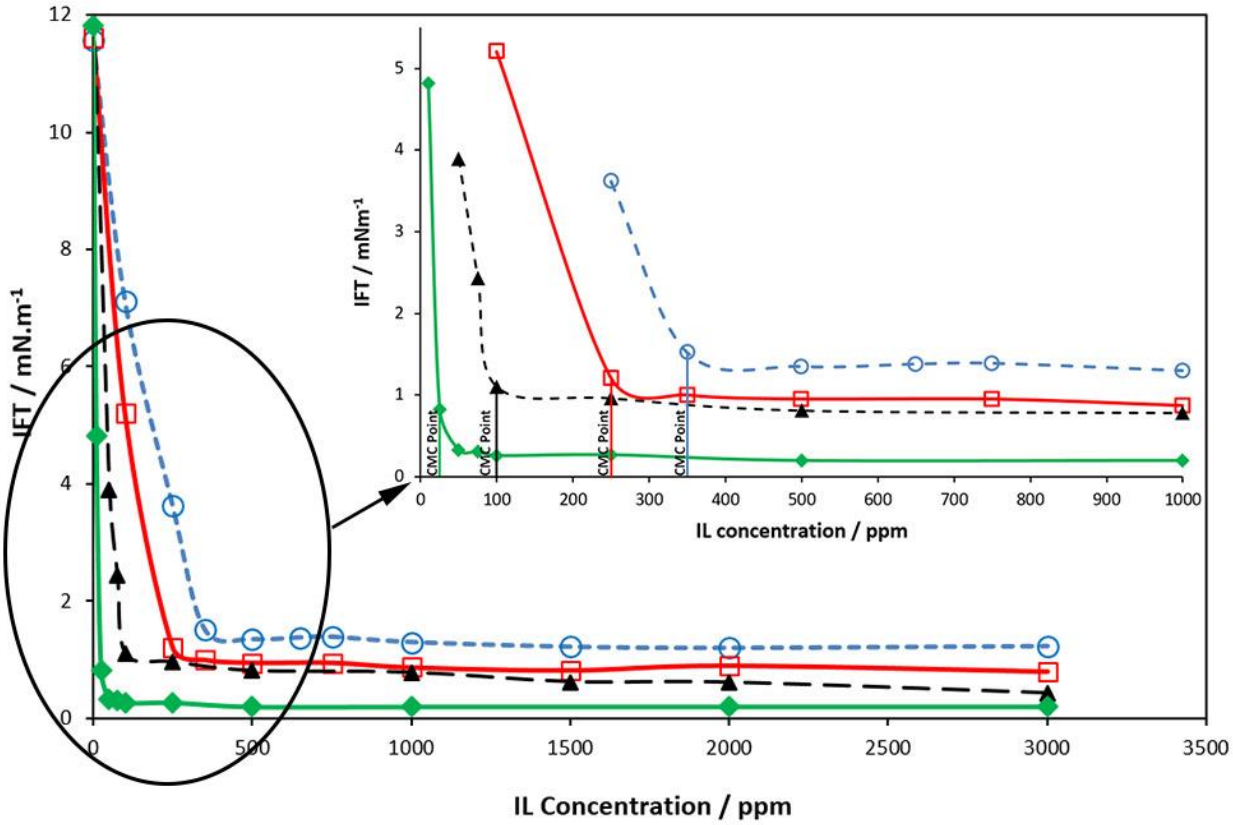


Fig. 5. Effect of ILs (containing chloride anion) concentration on the IFT of sea water and crude oil, (○) [C_8mim][THDP], (□) [C_{10}mim][THDP], (▲) [C_{12}mim][THDP] and (♦) [C_{14}mim][THDP]

Fig. 1. Experimental values of density, ρ (g/cm^3) against temperature (°C) for (●) ([C_8mim][Cl]), (♦) ([C_{10}mim][Cl]), (□) ([C_8mim][THDP]) and (×) ([C_{10}mim][THDP])

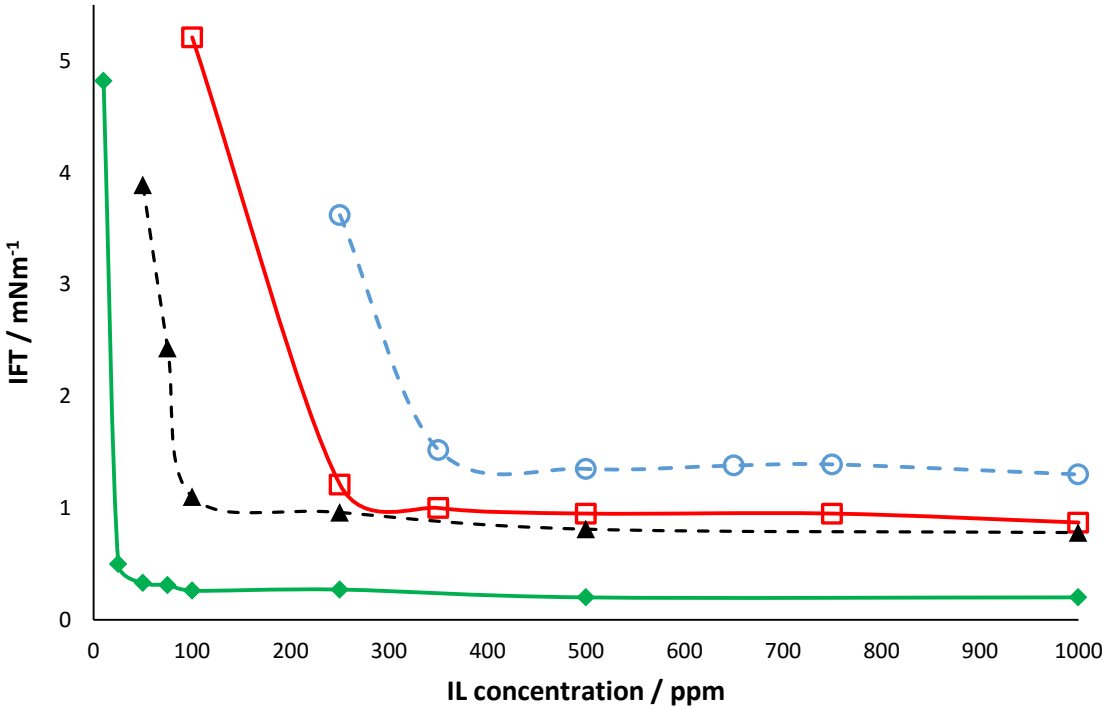
Fig. 2. Experimental values of viscosity η (mpa.s) against temperature (°C) for (●) ([C_8mim][Cl]), (♦) ([C_{10}mim][Cl]), (□) ([C_8mim][THDP]) and (×) ([C_{10}mim][THDP])

Fig. 3. Experimental values of refractive index n_D, against temperature (°C) for (●) ([C_8mim][Cl]), (♦) ([C_{10}mim][Cl]), (□) ([C_8mim][THDP]) and (×) ([C_{10}mim][THDP])

Fig. 4. Effect of ILs (containing chloride anion) concentration on the IFT of sea water and crude oil, (●) [C_8mim][Cl], (■)[C_{10}mim][Cl], (Δ) [C_{12}mim][Cl] and (×) [C_{14}mim][Cl]

Fig. 5. Effect of ILs (containing chloride anion) concentration on the IFT of sea water and crude oil, (○) [C_8mim][THDP], (□) [C_{10}mim][THDP], (▲) [C_{12}mim][THDP] and (♦) [C_{14}mim][THDP]

Graphical Abstract



Highlights

1- Four new ILs containing trihydrogen diphosphate anion, were synthesized and characterized for the first time.
2- The used ILs had significant efficiency in reducing interfacial tension in water injection process.
3- As the alkyl chain was longer, the CMC point and IFT value were more reduced.
4- These ILs are favorable choices in economic circumstances due to their very low consumption.