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# Enhancement of Efficiency of Water Removal from Bangestan Crude Oil by Silica Nanoparticles Using Imidazolium-based Ionic Liquids

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## Abstract

The effect of coating silica nanoparticles by several 1-alkyl-3-methylimidazolium hexafluorophosphate ionic liquids of [Rmim][PF6] general formula (R= $C_{10}$, $C_{12}$, and $C_{14}$) on the water removal efficiency of silica nanoparticles from crude oil emulsions have been studied in this study. The ionic liquids have been prepared and characterized by comparing their 1HNMR and FT-IR spectra with those reported in the literature. In addition, the effects of factors including cation alkyl chain length and concentration of the ionic liquids prepared on the water separation efficiency of the demulsifier have also been investigated to determine the optimal values for the chain length and concentration of the ionic liquid. [$C_{14}$mim][$PF_6$] ionic liquid at a concentration of 1200 ppm was shown to be the most efficient ionic liquid among the ionic liquids studied. The water separation efficiency achieved using coated nanosilica under optimal conditions was 93.3%.

***Keywords:*** Ionic Liquids, Demulsification, Crude Oil, Silica Nanoparticles.

## Introduction

One of the major problems in the petroleum industry is the presence of water in crude oil. Some of the water usually settles out rapidly as free water, but the rest of the water droplets are dispersed as resin, asphaltene, wax, and naphthenic acid. It is necessary to separate water from crude oil emulsions before transportation and refining due to economic and operational reasons to prevent corrosion in pipelines and equipment and the poisoning of catalysts in the refinery processes [1-3].

Iranian crude oil is heavy due to the presence of high molecular weight compounds and heavy metals. Therefore, the emulsion of water in oil is very stable and difficult to break. In addition to high molecular weight compounds in crude oil, temperature, pH, water droplet size, viscosity, interfacial tension, and difference in density between the two phases are considered the other important parameters in this regard [4-6].

There are several techniques for demulsification, including pH adjustment, gravity settling, filtration, and the addition of chemical demulsifiers, which are surface-active agents developing high surface tension at the oil-water interface. The most conventional method for breaking water in crude oil emulsions is the application of demulsifiers [1-5]. Demulsifiers destroy the stable film around the water droplets to yield water-free crude oil [7]. Commercial demulsifiers include propylene oxides of alcohols and ethylene copolymers, ethoxylated alcohols, amines, resins, alkylphenols, polyethylene amine, and dedecabenzenesulfonic acid have been extensively used for this purpose. For example, the application of conventional demulsifiers such as ethylene oxide-propylene oxide block copolymers to separate water from crude oil has been previously reported [1-3, 4].

The maximum demulsification efficiency using demulsifiers is usually evaluated by studying the effect of temperature, pH, settling time, mixing time, demulsifier concentration, and dilution rate on the water removal process [1-3, 7-8]. However, conventional demulsifiers are environmentally hazardous chemicals, and thus there are important drives for developing environmentally benign compounds to replace the currently used chemicals [9]. One such "green" chemical is ionic liquids. Ionic liquids (ILs) have unique properties such as non-volatility, non-flammability, thermal stability, being liquid at room temperature, and good solvation characteristics, which can be adjusted to meet the requirements of particular processes [10-11]. Ionic

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liquids have previously been used for separation purposes. For example, 1-ethyl-3-methylimidazolium ethyl sulfate [Etmim][$EtSO_4$], 1,3-dimethyl imidazolium methyl sulfate [Mmim][$MeSO_4$], and 1-octyl-3-methylimidazolium nitrate [Omim][$NO_3$] ionic liquids have been used in thermal-oxidative desulfurization of model fuel oils containing 500 ppm benzothiophene (BT) and dibenzothiophene (DBT) solutions in dodecane. The efficiency of sulfur removal from BT and DBT solutions by these ILs and the effect of anion and cation chain length have also been investigated [12]. In addition, aromatic and aliphatic compounds have reportedly been separated by ionic liquids [13-14]. Some ILs reduce the interfacial tension (IFT) of water/oil systems and may contribute to emulsion destabilization [15]. Imidazolium-based, which contain a positively charged head and an alkyl chain as the tail ILs, are demulsifiers with amphiphilic characteristics [15-17]. On the other hand, nanomaterials such as nano titania and nanosilica have been recently applied to improve the performance of chemical demulsifiers. As known, solids make the interfacial layer strong and improve emulsion stability. The application of nanoparticles along with demulsifiers is reported to improve the efficiency of the demulsifiers and increase water separation [18-20]. For example, Gandomkar et al. used nanosilica coated with polyalcohols to enhance the demulsification efficiency. They reported that coating nanosilica with a hydrophobic compound caused the nanoparticle to penetrate through the interfacial layer and destroy it, thus improving the demulsification efficiency by up to 40% [21].

The objective of this study was to use a series of ILs and compare the effect of cation alkyl chain and concentration on their demulsification efficiency. The ILs with the highest water removal efficiency were then used to coat silica nanoparticles, and the silica nanoparticles' demulsification efficiency was investigated.

## Materials and Methods

All chemicals were purchased from Sigma Aldrich and Merck Chemical Co. and used without further purification, except for 1-methylimidazole, which was purified by refluxing over KOH pellets at reduced pressure. The characteristics of the nanosilica particles were 4860MR- $SiO_2$ and 99.5% APS 20 nm, BET 160 $m^2/g$.

The crude oil sample was obtained from the Bangestan oil field in Ahwaz, Iran. In Table 1, the characteristics of the crude oil are shown.

**Table 1** Characteristics of Bangestan crude oil.

| Physical characterization | | |
|---|---|---|
| Type of characterization | Value | Standard Test Method |
| API gravity @ 15°C | 31.63 | ASTM D1298 |
| (cSt) Kinematic viscosity @15ºC | 16.71 | ASTM D7042 |
| (g/ml) Density @ 15°C | 0.8674 | ASTM D4052 |

The specifications of the silica nanoparticles used in this study are shown in Table 2.

$^1$H NMR spectroscopy was carried out using a Bruker 300 spectrometer (300 MHz) in $CD_3CN$ solvent using TMS as the internal standard. A Mattson 1000 FTIR spectrophotometer was used to record FTIR spectra using KBr disks in the 400-4000 $cm^{-1}$ range.

**Table 2** Specifications of the $SiO_2$ nanoparticles.

| | |
|---|---|
| Assay | 99.5% Trace Metals Basis |
| Particle size | 10-20 nm (BET) |
| Boiling point | 2230 °C |
| Melting point | >1600 °C |
| Density | 2.2-2.6 g/mL at 25 °C |
| Bulk Density | 0.011 g/mL |

A UP 400S Hielscher ultrasonic processor was used for sample dispersion. An Ohaus GT 8000 analytical balance, a Haake N3 thermostat water bath, a NORMALAB oil test centrifuge, and 100-1000 µL Transferpette or 0.5-100 µL Dragon Lab micropipettes were used during the experiments. The initial water content of the crude oil samples, the amount of water separated upon addition of the demulsifier, and the initial salt content were determined using the Standard Test Method for Water in Petroleum Products and Bituminous Materials by Centrifuge Method (ASTM D-4007) and bottle test using standard, graduated, 100 mL conical bottles (DURAN 50, Germany).

1-alkyl-3-methylimidazolium-based ILs were synthesized in a two-step process. In the first step, intermediate 1-alkyl-3-methylimidazolium halides were prepared by reacting the corresponding 1-alkyl halide and 1-methylimidazole. The intermediate ILs thus obtained were then reacted with hexafluorophosphate via metathesis to synthesize the other ILs.

General Method for the Synthesis of 1-alkyl-3-methylimidazolium Halides [Rmim][X].

A mixture of 1-methylimidazole and 1-alkyl chloride (1:1.1 molar ratio) was refluxed in a round-bottomed flask equipped with a reflux condenser under N2 flow for 22 h at 115 °C. The product was washed with refluxing ethyl acetate to remove any traces of unreacted starting materials, and the pure product was then heated for 7 hours at reduced pressure at 70 o C to dry [10-11]. The product yields ranged from 88.9 to 95.0%. The product's purity was confirmed by comparing their 1HNMR and FT-IR spectral data with literature values.

General Method for Metathesis Reactions

To an aqueous solution of 1-alkyl-3-methylimidazolium chloride, a solution of KPF6 in water was added (1:1.1 molar ratio) in a round-bottomed flask under a constant flow of N2, and the resulting suspension was vigorously stirred at room temperature for 10 hours. Upon completion of the reaction, the corresponding solid inorganic by-product (KCl) was removed by filtration. The product was washed several times with water and then dried in vacuo at 70 oC [10-11]. The product yields ranged from 68.0 to 97.0%. The products' purity was confirmed by comparing their 1HNMR and FT-IR spectral data with literature values. The 1HNMR spectral data for 1-alkyl-3-methylimidazolium ILs prepared are shown in Table 3:

## Preparation of Nanosilica Coated with Ionic Liquids

A mixture of nanosilica and the IL ([$C_{10}$mim][$PF_6$], [$C_{12}$mim][$PF_6$] or [$C_{14}$mim][$PF_6$]) (1:4 molar ratio) was dispersed in 10 mL of toluene for 3 hours under $N_2$ atmosphere at ambient temperature.

The product obtained was then filtered and dried in an oven at 50 °C for 4 hours [22-23]. Finally, FT-IR spectroscopy was used to characterize the products synthesized.

**Table 3** [1]HNMR spectral data for 1-alkyl-3-methylimidazolium ILs prepared.

| IL | $^1$H NMR spectral data |
|---|---|
| $C_{10}$mimCl | 9.76 (d, *J* = 33.3 Hz, 1H), 7.65 (dd, *J* = 22.7, 11.6 Hz, 2H), 4.30 – 4.09 (m, 2H), 4.01 – 3.77 (m, 3H), 2.06 – 1.82 (m, 2H), 1.87 – 1.64 (m, 2H), 1.19 (s, 12H), 0.80 (t, *J* = 6.6 Hz, 3H) |
| $C_{10}$mimPF$_6$ | 8.39 (s, 1H), 7.34 (dd, *J* = 17.6, 9.8 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 2.04 – 1.88 (m, 2H), 1.80 (d, *J* = 6.6 Hz, 2H), 1.28 (s, 12H), 0.87 (d, *J* = 7.0 Hz, 3H) |
| $C_{12}$mimCl | 9.68 (d, *J* = 31.5 Hz, 1H), 7.56 (dd, *J* = 19.8, 9.2 Hz, 2H), 4.20 (dd, *J* = 17.2, 9.9 Hz, 2H), 4.00 – 3.76 (m, 3H), 2.04 – 1.85 (m, 2H), 1.86 – 1.63 (m, 2H), 1.23 (s, 16H), 0.84 (t, *J* = 6.6 Hz, 3H) |
| $C_{12}$mimPF$_6$ | 8.51 (d, *J* = 15.3 Hz, 1H), 7.38 (dd, *J* = 6.2, 1.6 Hz, 2H), 4.11 (dd, *J* = 14.4, 7.1 Hz, 2H), 3.81 (d, *J* = 15.4 Hz, 3H), 1.99 – 1.86 (m, 2H), 1.84 – 1.72 (m, 2H), 1.21 (d, *J* = 16 Hz, 7H), 0.88 (t, *J* = 6.5 Hz, 3H) |
| $C_{14}$mimBr | 8.43 (d, *J* = 31.0 Hz, 1H), 7.38 (dt, *J* = 12.8, 1.8 Hz, 2H), 4.33 – 4.00 (m, 2H), 3.89 – 3.78 (m, 3H), 1.94 (tt, *J* = 13.5, 6.7 Hz, 2H), 1.81 (s, 2H), 1.29 (d, *J* = 8.9 Hz, 20H), 0.88 (t, *J* = 6.6 Hz, 3H) |
| $C_{14}$mimPF$_6$ | 8.29 (d, *J* = 17.8 Hz, 1H), 7.22 (dd, *J* = 27.5, 10.8 Hz, 2H), 4.01 (dd, *J* = 16.0, 8.7 Hz, 2H), 3.84 – 3.63 (m, 3H), 1.97 – 1.81 (m, 2H), 1.73 (s, 2H), 1.16 (d, *J* = 17.9 Hz, 20H), 0.78 (t, *J* = 10.9 Hz, 3H) |

**Preparation of Nanosilica Coated with Ionic Liquids in Ethanol/water (60/40) Solvent Mixture**

A mixture of nanosilica and [Rmim][PF$_6$] ILs (R= $C_{10}$, $C_{12}$, or $C_{14}$) (1:1 molar ratio) was dispersed in ethanol/water (60/40) solvent mixture by ultrasonication for 8 minutes, followed by mixing in a vacuum and atmospheric pressure for 5 and 1 hour, respectively, and then diluted to 25 mL in a volumetric flask using ethanol/water (60/40) solvent mixture [22-23]). The FT-IR spectral data of silica coated with different ionic liquids are shown in Table 4.

**Table 4** FT-IR spectral data for nanosilica particles coated with and [Rmim][PF$_6$] ILs.

| Compound | Wavenumbers (cm$^{-1}$) and peak assignments |
|---|---|
| [$C_{10}$mim][PF$_6$] + $SiO_2$ | 3431 (SiOH stretching), 3149 (C-H stretching alkene), 3080 (C-H stretching alkene), 2957 (-CH stretching alkane), 2927 (C=H stretching alkane), 2856 (C-H stretching alkane), 1631 (C=N stretching imine), 1573 (C=C stretching disubstituted), 1467 (C-H stretching methyl group), 1099 (C=N stretching amine), 799 (C=C bending alkene) |
| [$C_{12}$mim][PF$_6$] + $SiO_2$ | 3389 (SiOH stretching), 3147 (C-H stretching alkene), 3079 (C-H stretching alkene), 2959 (C-H stretching alkane), 2923 (C-H stretching alkane), 1630 (C=N stretching imine), 1572 (C=C stretching disubstituted), 1486 (C-H stretching methyl group), 1170 (C=N stretching amine), 846 (C-H bending disubstituted), 765 (C=C bending alkene) |
| [$C_{14}$mim][PF$_6$] + $SiO_2$ | 3426 (SiOH stretching), 3181 (CH stretching alkene), 2922 (C-H stretching alkane), 2852 (C-H stretching alkane), 1627 (C=N stretching imine), 1574 (C=C stretching disubstituted), 1468 (C-H stretching methyl group), 1099 (C=N stretching amine), 757(C=C bending alkene) |

**Bottle Test Procedure**

Standard, graduated, 100 mL DURAN 50 conical bottles (Germany) were used for bottle tests. To ensure the homogeneity of the crude oil sample to be tested, the oil was well shaken. Afterward, the crude oil was poured into the bottle up to the mark. Appropriate volumes of the emulsifier solutions or undiluted samples were injected into the bottle containing the crude oil sample using micropipettes with disposable plastic dispensers/heads.

The bottles were then capped with plastic stoppers and vigorously shaken in vertical and horizontal directions 100 times each. The bottles were placed inside metal baskets in sets of 12 and immersed in a thermostat water bath such that the liquid covered the entire crude oil inside the bath. The quantity of the water separated was measured and recorded at 15, 30, 60, 240, and 360 minutes. To ascertain the accuracy of the results, each test was performed in triplicate.

**Results and Discussion**

A series of ILs with unique typical characteristics, including non-volatility, non-flammability, thermal stability, being liquid at ambient temperature, and reasonable salvation properties, have been studied as environmentally friendly alternatives for currently used hazardous chemical demulsifiers. The efficiency of known ILs, namely, [$C_{12}$mim][PF$_6$], [C10mim][PF$_6$], and [$C_{14}$mim][PF$_6$] as demulsifiers in water removal from the Bangestan crude oil (Table 1) containing 15% water at the temperature of 60 oC has been investigated. Having selected the appropriate combination of solvents, the effects of two important parameters: the demulsifier concentration and the cation alkyl chain length of ILs, on the demulsification efficiency of the selected ILs have been studied.

**Solvent Selection**

Hexane, toluene, and water were tested as solvents. At first, 1-dodecyl-3-methylimidazolium hexafluorophosphate ([$C_{12}$mim][PF$_6$]) was dispersed in each of these solvents separately, and the stability of the dispersion obtained was observed after 7 minutes, 1 hour and 24 hours. Water was determined as the best solvent in terms of the stability of the dispersion, and minimum dispersion was observed in hexane. ILs have very low solubility in water. Therefore, toluene was used to prepare the solutions for bottle tests. However, following the preliminary investigations and based on the results obtained, an ethanol/water solvent mixture (60/40) was selected as the solvent to enhance the demulsification efficiency [21].

**Effect of Concentration**

The effect of demulsifier concentration in the 100-1200 ppm range on the water removal efficiency of [$C_{12}$mim][$PF_6$], [$C_{10}$mim][$PF_6$], and [$C_{14}$mim][$PF_6$] ILs from the Bangestan crude oil emulsions containing 15% water at 60 °C was first studied. IL solutions prepared in toluene were evaluated by the bottle test method. The amounts of water separated from the Bangestan crude oil emulsions containing 15% water at 60 o C were measured after 15, 30, 60, 240, and 360 minutes (Table 5 and Figure 1).

No or little separation was observed at [$C_{12}$mim][$PF_6$] concentrations of 100, 200, and 400 ppm. Maximum water separation was observed in the range of 800-1200 ppm with 80% water removal at a demulsifier concentration of 1200 ppm. In addition, increasing the concentration beyond 1600 ppm decreased water separation due to the decreased interfacial tension of oil and water, which reduces the demulsification efficiency. Therefore, the evaluations of [$C_{10}$mim][$PF_6$] and [$C_{14}$mim][$PF_6$] ILs were performed using concentrations in the range of 400-2000 ppm. Similar results were obtained in demulsification using identical concentrations (1200 ppm) of [$C_{10}$mim][$PF_6$] and [$C_{14}$mim][$PF_6$] ILs (60.0 and 93.3%, respectively). Therefore, the optimum demulsifier concentration under the test conditions was found to be 1200 ppm.

**Table 5** Average separated water (%) by different concentrations of [$C_{12}$mim][$PF_6$].

| Demulsifier Conc. (ppm) | Average Separated Water (%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 15 min. | 30 min. | 60 min. | 2 h | 4 h | 6 h | 24 h |
| 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 200 | 0 | 0 | 3.3 | 10.0 | 16.0 | 16.0 | 16.0 |
| 400 | 0 | 9.3 | 23.3 | 40.0 | 40.0 | 40.0 | 40.0 |
| 800 | 12.0 | 20.0 | 26.6 | 46.7 | 60.0 | 60.0 | 60.0 |
| 1200 | 20.0 | 33.3 | 53.3 | 66.7 | 80.0 | 80.0 | 80.0 |
| 1600 | 14.7 | 23.3 | 33.3 | 53.3 | 66.7 | 66.7 | 66.7 |
| 2000 | 3.3 | 16.0 | 23.3 | 33.3 | 40.0 | 40.0 | 40.0 |
| Blank | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

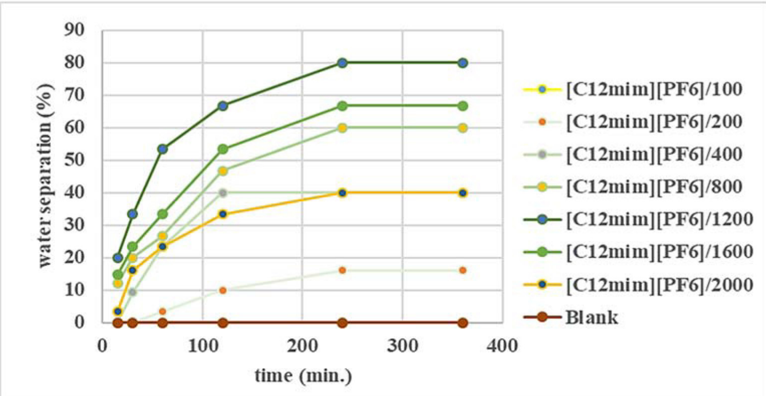


**Fig. 1** Water separation (%) by different concentrations of [$C_{12}$mim][$PF_6$] ionic liquid.

**Effect of Cation Alkyl Chain**

To determine the effect of cation alkyl chain length of the ILs on their demulsification efficiency from the Bangestan crude oil emulsions containing 15% water at 60oC, identical concentrations of [$C_{10}$mim][$PF_6$], [$C_{12}$mim][$PF_6$], and [$C_{14}$mim][$PF_6$]) (1200 ppm) were used in bottle tests. The results in Table 6 and Figure 2 indicate that increasing the alkyl chain length and, thus, the molecular weight of the ionic liquid increases the demulsification efficiency.

Therefore, more water separation is observed as the length of the alkyl chain increases. The maximum water removal percentages of [$C_{10}$mim][$PF_6$], [$C_{12}$mim][$PF_6$] and [$C_{14}$mim][$PF_6$]) ILs were 60.0, 80.0 and 93.33%, respectively.

**Table 6** Average separated water (%) by [$C_{10-14}$mim][$PF_6$] ILs.

| Demulsifier/Conc. (1200 ppm) | Average Separated Water (%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 15 min. | 30 min. | 60 min. | 2 h | 4 h | 6 h | 24 h |
| [$C_{10}$mim][$PF_6$] | 12.0 | 20.0 | 33.3 | 46.7 | 60.0 | 60.0 | 60.0 |
| [$C_{12}$mim][$PF_6$] | 20.0 | 33.3 | 53.3 | 66.7 | 80.0 | 80.0 | 80.0 |
| [$C_{14}$mim][$PF_6$] | 33.3 | 46.7 | 60.0 | 73.3 | 86.7 | 86.7 | 93.3 |
| Blank | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

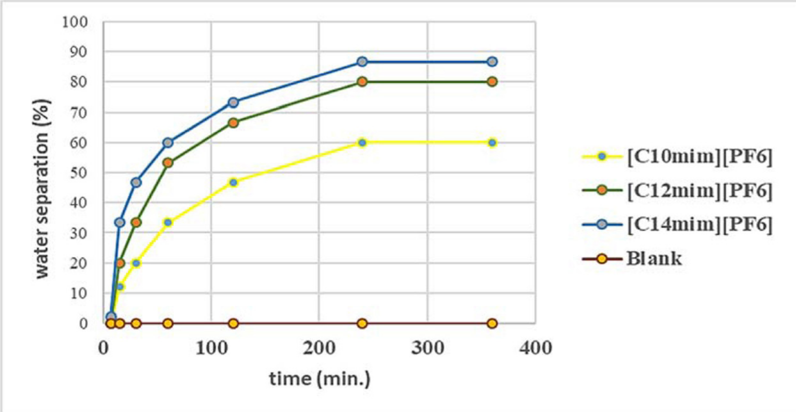


**Fig. 2** Effect of molecular weight on demulsification efficiency of $[C_{10-14}mim][PF_6]$ ILs

The demulsification efficiency of these ILs has been previously investigated by Hazrati et al. using a different crude oil [24]. In Table 7, the corresponding data using $[C_{12}mim][PF_6]$ are shown. The comparison of the demulsification performance by $[C_{12}mim][PF_6]$ ionic liquid in this study (Table 3) with the corresponding reported values indicates more water separation by the latter at the demulsifier concentration of 2000 ppm after 6 hours (82.5% vs. 40.0%). However, relatively good water separation (80%) has been obtained in this study at the demulsifier concentration of 1200 ppm.

**Table 7** Average separated water (%) reported by different concentrations of $[C_{12}mim][PF_6]$ [24].

| Demulsifier Conc. (ppm) | Average Separated Water (%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 15 min. | 30 min. | 60 min. | 2 h | 4 h | 6 h | 24 h |
| 500 | - | - | 70.0 | 78.75 | - | 81.25 | 82.5 |
| 2000 | - | - | 77.5 | 78.75 | - | 82.5 | 85.0 |
| 3500 | - | - | 66.25 | 72.5 | - | 72.5 | 75.0 |

## Nanosilica as Demulsifier

Nanosilica has also been used as a demulsifier. The investigation of the demulsification efficiency of nanosilica dispersions using crude oil emulsions containing 15% water at 60 °C in ethanol/water (60/40) indicated that no water separation occurred in the first two hours.

## Nanosilica Coated with Ionic Liquids as Demulsifiers

To enhance the demulsification efficiency of silica nanoparticles, they were coated with $[C_{10}mim][PF_6]$, $[C_{12}mim][PF_6]$, and $[C_{14}mim][PF_6]$ ILs.

The average separated water (%) values by nanosilica coated with $[C_{10}mim][PF_6]$, $[C_{12}mim][PF_6]$, and $[C_{14}mim][PF_6]$ ILs in ethanol/water (60/40) solvent mixture using crude oil emulsions containing 15% water at 60 °C are shown in Tables 8-10 and Figures 3-5.

**Table 8** Average separated water (%) by nanosilica coated with $[C_{10}mim][PF_6]$ ionic liquid in ethanol/water (60/40) solvent mixture.

| Demulsifier Conc. (ppm) | Average Separated Water (%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 15 min. | 30 min. | 60 min. | 2 h | 4 h | 6 h | 24 h |
| 500 | - | - | 70.0 | 78.75 | - | 81.25 | 82.5 |
| 2000 | - | - | 77.5 | 78.75 | - | 82.5 | 85.0 |
| 3500 | - | - | 66.25 | 72.5 | - | 72.5 | 75.0 |

**Table 9** Average separated water (%) by by nanosilica coated with $[C_{12}mim][PF_6]$ ionic liquid in ethanol/water (60/40) solvent mixture.

| Demulsifier/Conc. (ppm) | Average Separated Water (%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 15 min. | 30 min. | 60 min. | 2 h | 4 h | 6 h | 24 h |
| $[C_{10}mim][PF_6]$ + $SiO_2$/400 | 0 | 0.13 | 5.3 | 40.0 | 40.0 | 40.0 | 40.0 |
| $[C_{10}mim][PF_6]$ + $SiO_2$/800 | 0.33 | 13.3 | 33.3 | 46.7 | 46.7 | 46.7 | 46.7 |
| $[C_{10}mim][PF_6]$ + $SiO_2$/1200 | 13.3 | 23.3 | 40.0 | 50.0 | 63.3 | 66.7 | 66.7 |
| $[C_{10}mim][PF_6]$ + $SiO_2$/1600 | 12.0 | 20.0 | 40.0 | 46.7 | 60.0 | 60.0 | 60.0 |
| $[C_{10}mim][PF_6]$ + $SiO_2$/2000 | 0.33 | 3.3 | 5.3 | 8.0 | 13.3 | 13.3 | 13.3 |
| Blank | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

**Table 10** Average separated water (%) by nanosilica coated with [C14mim][PF6] ionic liquid in ethanol/water (60/40) solvent mixture.

| Demulsifier/Conc. (ppm) | Average Separated Water (%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 15 min. | 30 min. | 60 min. | 2 h | 4 h | 6 h | 24 h |
| [$C_{12}$mim][$PF_6$] + $SiO_2$/400 | 3.3 | 13.3 | 30.0 | 53.3 | 53.3 | 53.3 | 53.3 |
| [$C_{12}$mim][$PF_6$] + $SiO_2$/800 | 18.7 | 26.7 | 40.0 | 60.0 | 73.3 | 73.3 | 73.3 |
| [$C_{12}$mim][$PF_6$] + $SiO_2$//1200 | 23.3 | 40.0 | 56.7 | 73.3 | 80.0 | 80.0 | 86.7 |
| [$C_{12}$mim][$PF_6$] + $SiO_2$/1600 | 17.3 | 26.7 | 46.7 | 60.0 | 60.0 | 60.0 | 60.0 |
| [$C_{12}$mim][$PF_6$] + $SiO_2$/2000 | 5.3 | 17.3 | 26.7 | 40.0 | 46.7 | 46.7 | 46.7 |
| Blank | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

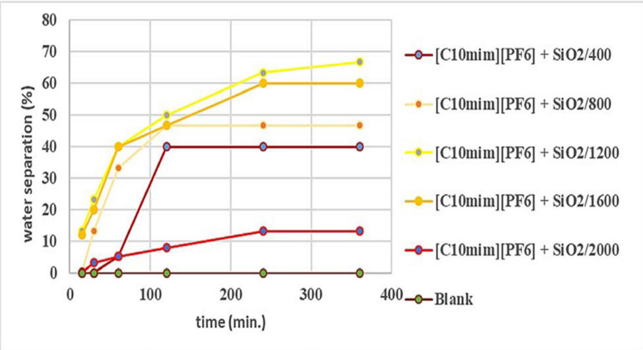


**Fig. 3** Water separation by nanosilica coated with [$C_{10}$mim][$PF_6$] ionic liquid in ethanol//water (60/40) solvent mixture.

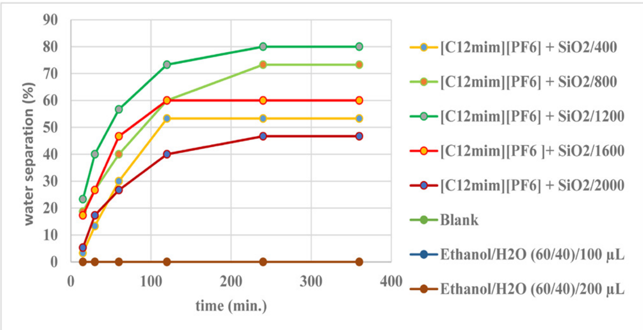


**Fig. 4** Water separation by nanosilica coated with [$C_{12}$mim][$PF_6$] ionic liquid in ethanol/water.

As observed, in all cases, increasing the demulsifier concentration increased the water removal percentage up to the concentration of 1200 ppm, after which the trend of water

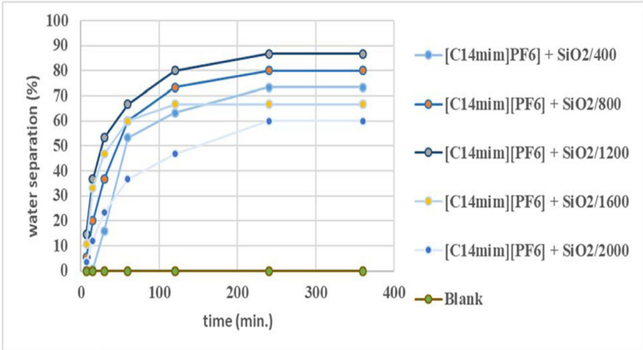


**Fig. 5** Water separation by nanosilica coated with [$C_{14}$mim][$PF_6$] ionic liquid in ethanol//water (60/40) solvent mixture.

removal reversed. The demulsification efficiency of nano silica coated with ILs is of the following order: [$C_{14}$mim][$PF_6$] + $SiO_2$ > [$C_{12}$mim][PF6] + $SiO_2$ > [$C_{10}$mim][$PF_6$] + $SiO_2$

Thus, nano-silica coated with [$C_{14}$mim][$PF_6$] ionic liquid showed the best demulsification efficiency.

Table 11 shows the comparison of the demulsification efficiency of [$C_{10}$mim][$PF_6$], [$C_{12}$mim][$PF_6$], and [$C_{14}$mim][$PF_6$] ILs with those of silica nanoparticles coated with these ILs at a temperature of 60 °C and the optimal concentration 1200 ppm.

As observed, in all the cases, coating nano silica with ILs improved the demulsification efficiency in the first 30 minutes (60 minutes in the case of [$C_{10}$mim][$PF_6$]). In other words, more water separation was obtained in shorter times by coating silica nanoparticles with these ILs.

**Table 11** Comparison of average separated water (%) by [$C_{10-14}$mim][$PF_6$] ILs with those of [$C_{10-14}$mim][$PF_6$] + $SiO_2$ at 1200 ppm concentration.

| Demulsifier/Conc. (1200 ppm) | Average Separated Water (%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 15 min. | 30 min. | 60 min. | 2 h | 4 h | 6 h | 24 h |
| [$C_{10}$mim][$PF_6$] | 12.0 | 20.0 | 33.3 | 46.7 | 60.0 | 60.0 | 60.0 |
| [$C_{10}$mim][$PF_6$] + $SiO_2$ | 13.3 | 23.3 | 40.0 | 50.0 | 63.3 | 66.7 | 66.7 |
| % improvement | 10.8 | 16.5 | 21.0 | 7.1 | 5.5 | 11.2 | 11.2 |
| [$C_{12}$mim][$PF_6$] | 20.0 | 33.3 | 53.3 | 66.7 | 80.0 | 80.0 | 80.0 |
| [$C_{12}$mim][$PF_6$] + $SiO_2$ | 23.3 | 40.0 | 56.7 | 73.3 | 80.0 | 80.0 | 86.7 |
| % improvement | 16.5 | 20.1 | 6.9 | 9.9 | - | - | 8.4 |
| [$C_{14}$mim][$PF_6$] | 33.3 | 46.7 | 60.0 | 73.3 | 86.7 | 86.7 | 93.3 |
| [$C_{14}$mim][$PF_6$] + $SiO_2$ | 36.7 | 53.3 | 66.7 | 80.0 | 86.7 | 86.7 | 93.3 |
| % improvement | 10.2 | 14.1 | 11.2 | 8.4 | - | - | - |

## Conclusions

The demulsification efficiency of 1-alkyl-3-methylimidazolium-based ILs of [Rmim][$PF_6$] general formula (R= $C_{10}$, $C_{12}$, and $C_{14}$) has been studied. The investigation of the effects of demulsifier concentration and cation alkyl chain on the demulsification efficiency of ILs using the Bangestan crude oil indicated that the optimal demulsifaction conditions were obtained using [$C_{14}$mim][$PF_6$] at the concentration of 1200 ppm at the temperature of 60oC. The comparison of the demulsification efficiency of [$C_{12}$mim][$PF_6$] IL used in this work with that of the identical IL previously reported using a different crude oil indicated more water separation by the latter at 2000 ppm demulsifier concentration after 6 hours (82.5% vs. 40.0%). Nevertheless, relatively good water separation (80%) has been obtained in this work at the demulsifier concentration of 1200 ppm.

[$C_{10}$mim][$PF_6$], [$C_{12}$mim][$PF_6$], and [$C_{14}$mim][$PF_6$] ILs have also been used to coat silica nanoparticles, which do not remove any water in the first 2 hours in order to enhance the demulsification efficiency of nano silica. The optimal water separation efficiency of 80% was obtained using nanosilica coated by [$C_{14}$mim][$PF_6$] ionic liquid.

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