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Full Length Article

Demulsification of water in crude oil emulsion using long chain imidazolium ionic liquids and optimization of parameters

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ABSTRACT

In this work, the application of ionic liquids in separation of water from crude oil as a water demulsifier was reported. Imidazolium ionic liquids substituted with long alkyl chains (n = 10, 12 and 14) were synthesized and used as surface-active demulsifiers which were coupled with Cl, PF_6 and NTf_2 anions. A full factorial design was performed for optimizing the behavior of demulsifiers based on three factors, *i.e.* alkyl chain length of cation, anion type and IL dosage in three levels. The measurements of interfacial tension between crude oil and water were done for each run and, the bottle test was carried out after demulsification process within the time intervals of 1, 2, 6 and 24 h. The optimal results for water separation efficiency and interfacial tension (IFT) were obtained 86–95% and 0.7–6.26 mN/m, respectively. The IFT reduction results showed that the studied ILs can be good candidates in enhanced oil recovery. It was found that increasing the ionic liquid hydrophobicity could significantly improve the demulsification efficiency along with IFT reduction. In hydrophobic ILs, it was indicated that increasing the alkyl chain length might improve the results, thus $[C_{14}mim][NTf_2]$ showed the best results in the bottle test as well as IFT reduction to 0.8 mN/m with 2000 ppm. The changes in droplet size were monitored by optical microscopy.

1. Introduction

As one of the major issue of petroleum industry, separation of water from crude oil emulsions has been considered for decades due to the viscosity increase of crude oil caused by emulsion droplets, which may consequently lead to higher pumping costs [1]. Intimate contact between aqueous and oily phase leads to the surfactant accumulation in the oil-water interface, followed by formation of a strong and rigid film which surround water droplets and resist droplet coalescence [2]. However, in the presence of naturally occurring interfacial active agents, such as asphaltenes, resins and oil-soluble organic acids (*e.g.*, naphthenic acids), very stable emulsions can be formed [3].

Completely separated crude oil and water emulsions are of necessity required before further transportation and processing. An appropriate chemical demulsifier and heating could facilitate the destabilization process [4]. It may be followed by a settling time to promote gravitational separation which turns it to the most widely applied and effective method of emulsion breaking. Chemical additives are widely used as destabilizer of emulsifying films around water droplets to get water-free crude oil.

In practice, commercial demulsifiers such as polymeric surface active additives containing polyoxyethylene, polyoxypropylene, dodecylbenzensulfonic acid, or blends of different surfactants are highly used [5]. Recent studies have been revealed the efficiency of graphene oxide [6–9], magnetic micro particles [10], cellulose based agents [11] and ionic liquids [12,13,9,14] as demulsifiers for separating water from crude oil emulsion.

Ionic liquids (ILs), the salts at liquid state, have unique physicochemical properties such as high thermal stability and low vapor pressure that make them suitable in various task-specific applications. ILs have also poorly coordinated organic cations to organic or inorganic anions, which leads to the melting points below 100 °C [15]. Introducing ILs to the W/O emulsion, it may result in migration of ILs to the oil/water interface, debilitation of the rigid surrounding film, and finally reduction of the interfacial tension between water and crude oil. Therefore, ILs as the good candidates can be studied to neutralize the stabilizing effect of emulsifying agents to facilitate resolving the emulsion. Evaluation of emulsion-breaking performance of different ILs was reported scarcely in crude oil [16,17,13]. It was indicated that ILs could be successfully applied as demulsifiers of high stable water-in-crude oil emulsions.

Although water separability of demulsifier depends on their

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structure and hydrophobic/hydrophilic properties, the nature and composition of the studied crude oil is also a substantial parameter [18]. Therefore, it is needed to tune the ILs structure for a variety of matrices and different application aspects. Moreover reduction of interfacial tension by ILs along with high thermal stability is interesting feature in enhanced oil recovery technique. This advantage leads to a wide study in performance of ILs in EOR [19–21].

The aim of this work is to compare efficiencies of tunable ILs in terms of cation and anion structure using experimental design and monitor the demulsification efficiency by optical microscopy and go beyond what was achieved previously.

2. Experimental

2.1. Materials

Methylimidazole, chloroalkane, potassium hexaflourophosphate, lithium bis(trifluoromethanesulphonyl) imide and all of the solvents were purchased from Merck (Germany). Methylimidazole and chloroalkane were distilled before the synthesis and the other chemicals were used as received.

The crude oil sample was obtained from one of the oilfields located at the south of Iran (Table 1). The composition of the formation brine is given in Table 2.

$Zn(acac)_2$

2.2. Emulsion preparation

The heavy crude oil and formation brine were both heated to 60 °C in water bath for 30 min to reduce the crude oil viscosity. The formation brine was then added to the crude to obtain a water content of 20% (v/v). The emulsion was prepared based on previously reported procedure in literature [16,17,13], using homogenizer (IKA, Ultra Turrax T25 Basic) in a mixing rate of 10,000 rpm and for 5 min yielding stable emulsions with droplet size between 11 and 16 μm (measured under optical microscope). The prepared emulsion with this procedure had no separation for weeks.

2.3. Synthesis of ionic liquids

Herein three long-alkyl-chain imidazolium cations were incorporated with three anions namely chloride (Cl), hexafluorophosphate (PF_6) and bis(trifluoromethanesulphonyl) imide (NTf_2) to synthesis of nine ionic liquids. ILs with chloride anion were hydrophilic, while PF_6 and NTf_2 -based ionic liquids were water immiscible.

According to a similar procedure previously reported [22], 1-alkyl-3-methylimidazolium chloride ILs were synthesized by reacting 0.1 mol methyl imidazole with 0.11 mol of 1-chloroalkane (chlorodecan, chlorododecan, chlorotetradecan) in a round-bottomed flask with a reflux condenser stirring for 72 h in 343.15 K under nitrogen atmosphere. The viscous liquid product was washed with diethyl ether to remove unreacted materials and dried in 333.15 K under vacuum. The synthesized 1-decyl-3-methylimidazolium chloride, 1-dodecyl-3-methylimidazolium chloride and 1-tetradecyl-3-methylimidazolium chloride ILs are abbreviated $[C_{10}mim][Cl]$, $[C_{12}mim][Cl]$ and $[C_{14}mim][Cl]$ respectively.

Table 1
General Properties of an Iranian heavy crude oil.

Experiments	Unit	Standard method	Results
API gravity at 15 °C		ASTMD1298	24.51
Viscosity at 15 °C	(mPa s)	ASTMD455	31.05
Wax content	(wt.%)	BP 237	5.4
Asphaltenes	(wt.%)	IP 143	2.80

Table 2
The formation brine composition.

Experiments	Unit	Results
pH		5.62
TDS	mg/L	254200
Ca	mg/L $CaCO_3$	52626
Mg	mg/L $CaCO_3$	20874
Na	mg/L	65600
Cl	mg/L	161000

Table 3
Experimental conditions and results of IFT and demulsification tests at 25 °C and 101 kPa.

Ionic Liquid	Dosage (ppm)	IFT (mN/m)	Demulsification Efficiency			
			1 h	2 h	6 h	24 h
Blank	0	13.57	0	0.5	0.5	0.75
$[C_{10}mim][Cl]$	500	2.73	87.5	87.5	90	93.75
	2000	2.87	86.25	86.25	87.5	92.5
	3500	3.25	77.5	77.5	80	85
$[C_{10}mim][NTf_2]$	500	3.11	75	82.5	87.5	93.75
	2000	0.81	95	100	100	100
	3500	0.7	95	100	100	100
$[C_{10}mim][PF_6]$	500	5.98	67.5	68.75	70	73.75
	2000	4.98	70	70	72.5	76.25
	3500	6.26	65	66.25	67.5	71.25
$[C_{12}mim][Cl]$	500	2.7	87.5	88.75	90	92.5
	2000	3.01	80	81.25	85	87.5
	3500	4.52	71.25	75	76.25	80
$[C_{12}mim][NTf_2]$	500	1.86	80	93.75	98.75	100
	2000	0.8	88.75	97.5	98.75	100
	3500	0.7	92.5	100	100	100
$[C_{12}mim][PF_6]$	500	4	70	78.75	81.25	82.5
	2000	3.7	77.5	78.75	82.5	85
	3500	5.02	66.25	72.5	72.5	75
$[C_{14}mim][Cl]$	500	3.36	76.25	77.5	78.75	82.5
	2000	3.45	75	75	77.5	80
	3500	4.89	67.5	67.5	71.25	76.25
$[C_{14}mim][NTf_2]$	100	1.93	83.5	90.0	92.2	93.6
	500	1.15	97.5	100	100	100
	2000	0.8	98.75	100	100	100
	3500	0.8	98.75	100	100	100
$[C_{14}mim][PF_6]$	500	2.61	83.75	85	86.25	86.25
	2000	2.87	80	80	82.5	85
	3500	4.66	72.5	73.75	77.5	80

The synthesis of PF_6 and NTf_2 salts was accomplished in the second step involving the ion exchange reaction using potassium hexafluorophosphate and lithium bis(trifluoromethanesulphonyl) imide salts respectively. The reaction was performed in aquatic phase. 0.1 mol of $LiNTf_2$ or KPF_6 was dissolved in water and added dropwise to the solution of 0.1 mol chloride ionic liquids. Non-aqueous phase was separated after 15 min of vigorous stirring. Finally washed with water and dried in 333.15 K under vacuum. The final water-immiscible products were 1-decyl-3-methylimidazolium hexafluorophosphate $[C_{10}mim][PF_6]$, 1-dodecyl-3-methylimidazolium hexafluorophosphate $[C_{12}mim][PF_6]$, 1-tetradecyl-3-methylimidazolium hexafluorophosphate $[C_{14}mim][PF_6]$, 1-decyl-3-methylimidazolium bis(trifluoromethanesulphonyl) imide $[C_{10}mim][NTf_2]$, 1-dodecyl-3-methylimidazolium bis(trifluoromethanesulphonyl) imide $[C_{12}mim][NTf_2]$ and 1-tetradecyl-3-methylimidazolium bis(trifluoromethanesulphonyl) imide $[C_{14}mim][NTf_2]$.