PERFORMANCE ENHANCING OF BLENDED IONIC LIQUIDS AS DEMULSIFIERS FOR WATER IN OIL EMULSIONS

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ABSTRACT

The main objective of this work is to investigate the role of two types of ionic liquids, 1-hexyl-1-methylimidazoliumtetrafluoroborate ([HMIM]BF$_4$), 1-hexyl-1-methylimidazoliumhexafluoro phosphate ([HMIM]PF$_6$), and blends of both ionic liquids upon the microwave demulsification process of water in crude oil emulsions. A series of batch demulsification runs were carried out to evaluate the final water content of emulsion samples after the exposure to microwaves at specified ionic liquid concentrations. Tests were also performed to find the effect of blending ionic liquids at various ratios on the demulsification efficiency. Results showed that, increasing the concentration of each ionic liquid yields improved demulsification results. In these tests, for similar mass concentrations of ILs, higher separation efficiencies were obtained when using [HMIM]PF$_6$. The performance of the less efficient ionic liquid [HMIM]BF$_4$ was significantly enhanced when it was blended with equal amount of [HMIM]PF$_6$.

Keywords: Demulsification, Microwave radiation, water-in-oil emulsion, ionic liquids, blends of demulsifiers

INTRODUCTION

Crude oil produced from geological formations can contain various amounts of water. Water and crude oil are naturally non-miscible; however, when naturally occurring, interfacial active compounds are present; these compounds can aggregate on the oil and water interface and cause water to form droplets within the bulk oil phase. During crude oil lifting through production tubing, the oil and water encounters an increased mixing energy from rapid flow through chokes and bends. This additional mixing energy can emulsify the oil and water. Such oil external, water internal two-phase system is commonly referred to as a crude oil emulsion, which can be quite stable.(Kokal, 2005; Nguyen, 2013).

The crude oils should be desalted and dewatered before refining because salts produce enormous corrosion problems, they are poison for the catalysts in refining and reduce the efficiency of energy exchanging, and increase the oil flow resistance and even obstruct the pipes. The process of desalting in oil refining process usually involves addition 1–20 wt% of wash water to the crude oil, mixing to form a W/O emulsion and then subjecting the emulsion to electrostatic demulsification or hydrocyclone treatment (Goyal, 1993, Varadaraj et al., 2001). Most crude oils that contain asphaltenes and naphthenic acids, especially heavy crude oils tend to form stable W/O emulsions, which are complex scattered systems (Kumar et al., 2001).
Chemical demulsification by adding surfactant demulsifiers is still one of the most frequently applied industrial method to break the crude oil emulsions (Sjoblom et al., 2001). This process can be very difficult and non-efficient to demulsify W/O emulsions of heavy viscous crude oils, and it takes a long time.

Commercial demulsifiers are polymeric surfactants such as block copolymers of polyoxyethylene (EO) and polyoxypropylene (OP) or alkylphenol-formaldehyde resins, or blends of different surface-active compounds and poly functionalized amines with EO/PO copolymer (Kokal, 2005; Hirasaki et al., 2011). Other types of tested demulsifiers are polyglycol esters, low molecular weight resin derivatives, high molecular weight resin derivatives, sulfonates, polymerized oils and esters, alkanolamine condensates, oxyalkylated phenols and polyamine derivatives and fatty alcohol polyoxyethylene (Li et al., 2006).
The application of microwave irradiation to break a W/O emulsion was described for the first time in 1995 (Fang, 1995) and in the last decade has been studied by several research groups (Xia et al., 2002, Xia et al., 2004,Nour and Yunus, 2006, Fortuny et al., 2007). The dielectric heating is based on the interaction of matter with the electric field of incident radiation, causing the movement of ions and induced or permanent dipoles of molecules, which in turn produces simple heating. For the specific case of crude oil emulsions, microwaves basically interact with water molecules and dissolved salts and also with the polar compounds existing in the crude, which include resins and asphaltenes .A lot of

activities have been developed recently regarding the use of microwave irradiation for demulsification purposes. This is because the microwave irradiation offers a clean, inexpensive, and convenient method of heating, which often results in higher yields and shorter reaction times (Kappe et al., 2009; Noor et al., 2012).

It has been generally accepted that the microwave technology allows for the fast heating of emulsions, favoring the separation of crude oil emulsions into water and oil phases by thermal effects (Chang and Chen, 2002; Xia et al., 2004; Liaoyuan et al., 2006). Moreover, it is believed that the interaction of microwaves with the salts and polar species present in the emulsion may induce non-thermal effects, such as specific thermal profiles that favor the diffusion of chemical demulsifiers or the modification of the molecular structure of chemical species located at the interfacial film, favoring the emulsion destabilization (Fang et al., 1989).

According to Chang and Chen, 2002, Fortuny et al., 2007, Coutinho et al., 2008, and Mohammed and Saadon, 2013, the composition of the medium [including type and concentration of salt, pH, and water content (WC)] greatly influences the progress of demulsification during the microwave process because the dielectric properties of the emulsion are correlated with the composition.

An interesting alternative used in microwave-assisted processes is the change in the composition of the system through the use of specific compounds that have high dielectric properties, thus enhancing the absorption of radiation by the sample (Lemos el al. 2010).

Moreover, these additives can be chosen to act in not only the heating system but also the mechanisms involved in the process. In this direction, ionic liquids (ILs) have been widely used as additives in processes involving microwave heating. ILs are a specific class of molten salts with high dielectric properties, consisting of organic cations combined with anions of organic or inorganic nature. The chemical structure of ILs allows many combinations of anions and cations, enabling one to obtain compounds with properties quite varied, which means that tailor-made ILs can be produced for a given application. Their boiling point is always less than 100°C (Huddleston et al., 2001; Kadokawa, 2013).

In processes using microwave heating, ILs have been used as catalysts and solvents in various organic reactions, as agents to assist the microwave heating of low-polarity organic solvents, etc. (Hoffmann et al., 2003). Besides, even the IL synthesis can be carried out under microwave irradiation, which allows one to obtain compounds of higher purity, thus eliminating purification steps. Recently, ILs have been used in the petroleum industry, including mainly the extraction of aromatic, polyaromatic, and heteroaromatic compounds from samples of aliphatic hydrocarbons, oil, gasoline, fuel oil, and diesel (Cassol et al., 2007; Schmidt et al., 2008).

The interaction of ILs with petroleum fractions was investigated by Shi et al., 2008 and Boukherissa et al., 2009. Shi et al. presented a new process for removing naphthenic acids from oil based on the reaction of these acids with an alcoholic solution and imidazolium-type derivatives to synthesize an IL able to settle out of the oil phase by gravity. Boukherissa et al. reported the use of ILs as the inhibitors of the aggregation of asphaltenes in the crude. The authors pointed out that the stabilization of asphaltenes in ILs is promoted by hydrogen bonds or charge-transfer interactions. Such mechanisms can be customized for each type of oil by changing the anion and/or cation of the IL to tailor their properties to the type of asphaltene and oil.

The application of this type of IL as a surfactant in the microemulsion polymerization of methyl methacrylate and suspension polymerization of styrene has been shown in the work of Guerrero-Sanchez et al., 2007. Finally, the ILs involve a set of properties that are attractive to help demulsification of water-in-crude oil emulsions because these compounds have high dielectric properties, can interact with polar fractions of petroleum, and ultimately may have an affinity for the interface because of their amphiphilic nature. Ionic liquids have been shown to readily absorb microwave radiation through dipole-dipole and ionic conductance mechanisms giving rise to exceptionally efficient heating and rapid increase in temperature. Recently, ILs were described as demulsifier agents for W/O emulsions. Lemos et al., investigated the role of two type of ILs ([OMIM]BF_4 and [OMIM]PF_6) as demulsifier agents of high stable W/O emulsions in conjunction with microwave irradiation. The use of mixed salts to generate new composite ionic liquids ILs provides a facile means of readily tuning or tailoring the desired properties of ionic media. Despite this, very little information is available about how the structure of the selected ions and composition impacts the properties of salt mixtures. To explore this, the demulsification efficiency of two imidazolium-based ionic liquid mixtures has been investigated.

EXPERIMENTAL WORK

The demulsification tests applying microwave radiation were conducted using microwave oven (LG), which provides 1000 W. A 500 ml graduated cylindrical glass was used as sample container. Three thermocouples type (K) were connected to data logger and then connected to microwave oven as shown in Fig. 1.

Fig.1. Photograph of experimental apparatus

MATERIALS

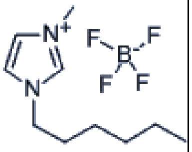
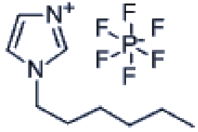
Light *Nafut Khana* crude oil used in this study was obtained from Middle Refinery Company in Iraq. The characteristics of crude oil are given in Table 1.

Table 1. Crude Oil Characteristics

Sp. Gr. At 15.6°C	0.8095
Density at 15.6˚C (gm/cm^3)	0.8091
API	40
Salt content (%wt.)	0.0013
Water content	Traces
Viscosity(poise)	0.0476

Two types of ionic liquids were used in this research, 1-hexyl-1 methylimidazoliumtetrafluoroborate [HMIM]BF_4, and 1-hexyl-1-methylimidazoliumhexafluorophosphate [HMIM]PF_6 supplied by Shanghai Chengjie Chemical Company. The physical properties of these ionic liquids are given in Table 2.

Table 2. Physical properties of ionic liquids

Characteristic	[HMIM]BF_4	[HMIM]PF_6
Structure		
Molecular Formula	$C_{10}H_{19}N_2BF_4$	$C_{10}H_{19}N_2PF_6$
Molecular Weight (g/mol)	254	312
Density (20°C g/cm^3)	1.1532	1.25
Melting Point (°C)	-81.85	-60.85
Refractive Index	1.426	1.4167
Viscosity(cp)	310	580

EMULSION PREPARATION

In this study, the microwave demulsification method was carried out using water-in-oil emulsion samples containing different water contents (8%, 15%, and 30%). Emulsions were agitated vigorously using a standard three blade propeller at constant speed of 3000 rpm for 45 minutes to facilitate the contact among the water droplets in the emulsion.

The prepared samples were tested for their stability under gravity at room temperature. The amount of water resolved is a measure of the emulsion stability. The system should not be separated into bulk oil and water phases after 3 days of gravity settling. The drop size distribution was measured using optical microscope model N117M with fitted 5Mp Digital Camera (Beijing NOVEL Optics Co., Ltd/China)

DEMULSIFICATION

A Set of demulsification experiments was conducted using [HMIM]BF_4 and [HMIM]PF_6 as chemical additives during tests conducted with microwaves, further microwave heating demulsification experiments were carried out under similar operating conditions but using three blends of both ionic liquids.

Tests were conducted at a temperature ranging from 61˚C to 81˚C with irradiation time of 50 seconds, microwave power of 1000 Watt and 3% salt content. Known amounts of IL (50, 150, 300, 500 ppm) were added to each emulsion sample prior to the test. Another set of experiments were conducted using three blends of both ionic liquids viz. (1:3, 1:1. 3:1).
After microwave irradiation, emulsion samples were put into graduated cylinders for settling measurements. The volumes of the separated water phase were recorded every 20 minutes for 3 hours. The separation efficiency (S) can be calculated from the following equation:

$$S\,\% = \frac{V_s}{V_0} \times 100\,\%$$ **.......... (1)**

Where:

S the separation efficiency

V_S the volume of separated water.

V_0 the original volume of water.

RESULTS AND DISCUSSION

1. The stability of the prepared emulsions

The stability of the prepared emulsions was measured by two methods, aging test and drop size distribution measurement by optical microscope. All emulsions stayed without clear separation for more than 6 months. Emulsions with different initial water contents (8%, 15%, 30%) have drop size of (5.5-7, 7-10, and 13-16) micron respectively for that these emulsions can be classified as tight emulsions

2. Effect of water content on demulsification efficiency

It is necessary to determine the relationship between dielectric properties and the water content in the emulsion, because the dielectric properties are influenced by the medium composition. This is especially important in demulsification processes, where water content variations are expected to occur. Besides emulsion water content can also influence the coalescence efficiency during the demulsification process, leading to reduced distance between droplets in the sample. This distance can be severely narrowed with the increase of the volume of the aqueous phase in the emulsion, raising the probability of collision between the droplets**.** From experimental results, it was observed that when the volume ratio of water is less, the emulsion is more stable. According to Fig.2, the increase of initial water content favors the coalescence between droplets and formation of free water.

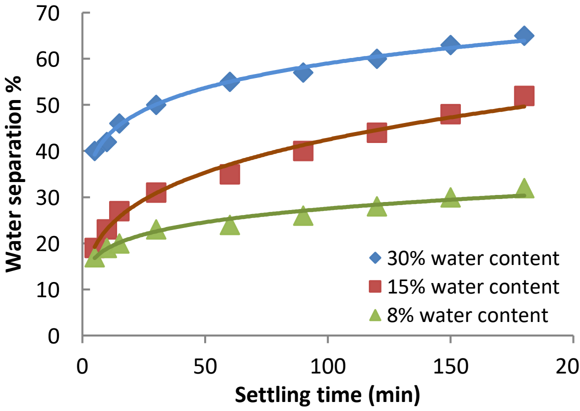


Fig.2. Effect of different volume ratios of w/o emulsion on the separation efficiency (irradiation power = 1000W, irradiation time =50 s, salt content = 3% NaCl)

3. Effect of ionic liquid dose on separation efficiency

Results showed that increasing the concentration of each IL yields improved demulsification results. Fig.3, shows that the separation efficiency increases from 35% for 50 ppm dose of [HMIM]PF₆ ionic liquid to 65% for 500 ppm dose after 180 min. settling.

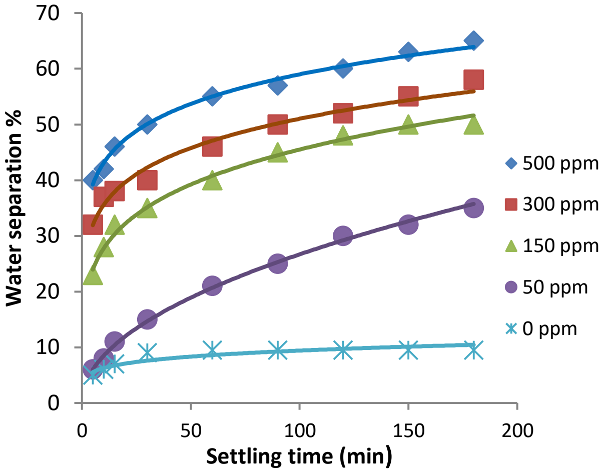


Fig.3. Effect of [HMIM]PF_6 ionic liquid dose on the separation efficiency (30% water content, irradiation power =1000W, irradiation time =50 s, salt content = 3% NaCl)

4. Effect of ionic liquid type on demulsification efficiency

In these tests, for similar mass concentrations of IL, higher separation efficiencies were obtained when using [HMIM]PF_6. According to the water separation measurements, it is shown from Fig.4, that [HMIM]PF_6 is able to promote a greater reduction in the water content of the system, besides possessing faster adsorption dynamics at the interface.

The HLB values of ionic liquids can be calculated from Griffin's mathematical method:

$$HLB = 20 \times \frac{M_H}{(M_H + M_L)} \quad \ldots\ldots\ldots\ldots \ (2)$$

Here M_H and M_L are molecular weights of hydrophilic and hydrophobic moieties, respectively. The values of HLB for [HMIM]BF_4 and [HMIM]PF_6 are (9.037) and (11.079) respectively. The solubility of demusifiers in water increases with increasing HLB values. The HLB values of both ionic liquids above testifying to good solubility.

It was found that the amount of water separated expressed as a percentage of coalescence increases with an increase in the HLB, this explains the higher demulsification efficiency of [HMIM]PF6. This finding may be explained in terms of the following factors:

- The increase in the HLB value increases the solubility of the surfactant in the aqueous phase (dispersed phase). When the demulsifier is initially introduced to the water-in-oil emulsion, it will be thermodynamically stable at the interface of the water droplets. Accordingly, the surfactants possessing high HLB migrate faster to the interface than those having low HLB. As a result of such enhanced migration toward the interface, the surfactant forms a continuous hydrophilic pathway between the dispersed water droplets. This leads to a rapture of the interfacial oil film surrounding the water droplets.

- Other properties not yet investigated for these ILs could play a role and then explain the superior ability of [HMIM]PF$_6$ on the demulsification process. In this regard, it could be due to the greater interaction of IL with polar species (resins and asphaltenes) located at the oil/aqueous phase interface, which could promote the desorption of species from the interface.

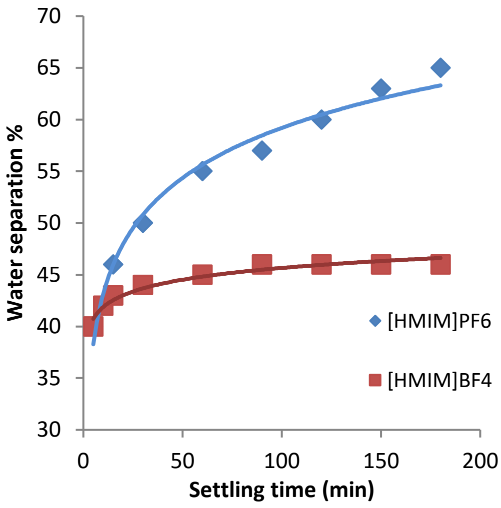


Fig.4. Effect of ionic liquid type on demulsification efficiency (500 ppm ionic liquid, 30% water content, irradiation power =1000W, irradiation time =50 s, 3% NaCl)

5. Enhancement of demulsification efficiency using blended ionic liquids

In order to optimize performance of the less efficient ionic liquid [HMIM]BF$_4$, it may be necessary to blend it with another ionic liquid. The best demulsifier formula for mixed materials is that gives hydrophilic and hydrophobic balance suitable for separating the W/O emulsion effectively. It is noted that separation efficiency changed remarkably with different blends ratios. When the ionic liquids in this work were blended together, different separation efficiencies were obtained, but the highest was recorded at (1:1) mixing ratio. This can be explained depending on the properties of the two ionic liquids used. The hydrophobic ionic liquid [HMIM] PF$_4$ would reach faster to the interfacial film surrounding water droplets to remove the asphaltenes - resin film partially and making holes in the film. At the same time, the hydrophilic [HMIM] BF$_4$ will reach inside water droplets through these holes and contributing in exploding drops to coalesce with other drops. As a result, the separation ratio will be higher than when ionic each liquid was used separately.

According to the HLB system, all crude oils have a required HLB. If it is required to demulsify certain crude oil emulsion, it would need to use demulsifier or blend of demulsifiers that had HLB of the same value as for the crude oil.

The value of HLB of blended ionic liquids can be determined from the following equation:

$$HLB_m = \sum_{i=1}^{n} x_i HLB_i \quad \ldots\ldots\ldots\ldots\ldots (3)$$

The demulsification process was improved when equal amounts of [HMIM]BF$_4$ and [HMIM]PF$_6$ were used during the tests as can be seen from Fig.5. The value of HLB_m for equal weight fraction of both ionic liquids is (10.058), which improve the demulsification process to reach (90%).

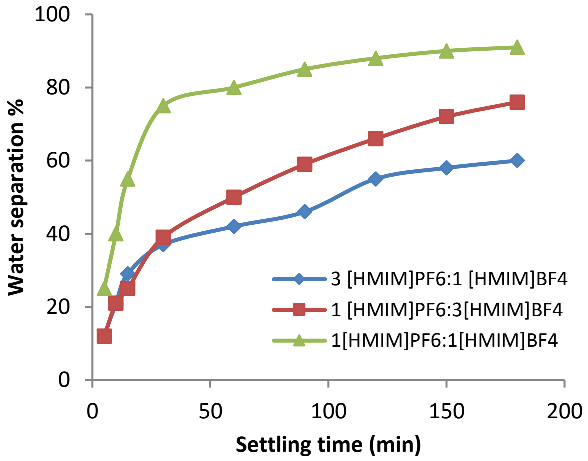


Fig.5. Effect of different mixture ratios of [HMIM]BF$_4$ and [HMIM]PF$_6$ on demulsification efficiency.

CONCLUSIONS

According to the results obtained from this study, the following conclusions are obtained:

- Improved separation efficiency for both ionic liquids tested was obtained for emulsions having higher water volume ratio due to the increase in electrical conductivity and energy dissipation per unit volume and therefore the heating effect.
- Increasing the dose of both ionic liquids used, yields improved demulsification results.
- The results showed that the combined use of microwave and ionic liquid [HMIM]PF6 allows high emulsion breaking efficiency.
- Mixed ionic liquid systems can offer significant improvements in the demulsification process.

NOMENCLATURE

HLB	Hydrophilic Lipophilic Balance (-)
M_H	Molecular weight of hydrophilic group (g/mol)
M_L	Molecular weights of hydrophobic (lipophilic) group (g/mol)
S	Separation efficiency (-)
V_o	Original volume of water (ml)

V_s Volume of separated water (ml)
x Weight fraction (-)

REFERENCES

Boukherissa M., F. Mutelet, A. Modarressi, A. Dicko , D. Dafri, and M. Rogalski. 2009. Ionic Liquids as Dispersants of Petroleum Asphaltenes, *Energy and Fuels, V.23 (5):* 2557–2564.

Cassol C., A. P. Umpierre, G. Ebeling. B. Ferrera, S. S. X. Chiaro, and J. Dupon. 2007. On the Extraction of Aromatic Compounds from Hydrocarbons by Imidazolium Ionic Liquids, *Int. J. Mol. Sci.* 8 : 593-605.

Chan C.C. and Y.C Chen. 2002. Demulsification of W/O Emulsions by Microwave Radiation, *J. Separation Sci. and Tech.* V.37 (15): 3407–3420.

Coutinho R.C., M.F. Heredia, M.N. de Souza, and A.F. Santos.2008.Method for the Microwave Treatment of Water-in-Oil Emulsions, *US Patent* : 0221226 A1.

Fang C.S., P.M.C. Lai, B.K.L. Chang and W.J. Klaila. 1989. Oil Recovery and Waste Reduction by Microwave Radiation. *Environ. Prog.* V.8(4): 235–238.

Fang C. S. and P. M. J. Lai.1995. Microwave-heating and separation of water-in-oil emulsion, *Journal of Microwave Power and Electromagnetic Energy* 30: 46-57.

Fortuny M., C. B. Z. Oliveira, R. L. Melo, , M. Nele, R. C. C. Coutinho and A. F. Santos.2007.Effect of Salinity, Temperature, Water Content, and pH on the Microwave Demulsification of Crude oil Emulsions, *Energy Fuels* 21: 1358-1364.

Goyal S. K., J. F. Mosby and J. E Treadman II. 1993.Removal of Metals and Water-Insoluble Materials from Desalter Emulsions, *US Patent* : 5219471.

Griffin, W. C.. 1954. Calculation of HLB Values of Non Ionic Surfactants, *J. Soc. Cosmetic Chemists* 5: 249.

Guerrero-Sanchez, C., M. Lobert, R. Hoogenboom, U.S. Schubert.2007. Microwave - Assisted Homogeneous Polymerizations in Water-Soluble Ionic Liquids: An Alternative and Green Approach for Polymer Synthesis, *Macromol. Rapid Commun.* 28: 456–464

Hirasaki G. J., A. M. Clarence, G. O. Raney, K. M. Poindexter, D. T. Nguyen. and J. Hera, 2011.Separation of Produced Emulsions from Surfactant Enhanced Oil Recovery Processes, *Energy Fuels,* V. 25(2): 555–561

Hoffmann J., M. Nuechter, B. Ondruschka, and P.Wasserscheid.2003.Ionic Liquids and their Heating Behavior during Microwave Irradiation, *Green Chemistry 5:* 296-299.

Huddleston J.G.; A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker and R.D. Rogers.2001.Characterization and Comparison of Hydrophilic and Hydrophobic Room Temperature Ionic Liquids Incorporating the Imidazolium Catio, *Green Chemistry* 3:156-164.

Kadokawa Jun-ichi.2013.Ionic Liquids-New Aspects for the Future*, In-Tech, Rijeka, Croatia*.

Kappe C. Oliver, D. Dallinger and S. S. Murphree. 2009. Practical Microwave nSynthesis for Organic Chemists*, Wiley-Vch Verlag Gmbh & Co. Kgaa، Weinheim. Germany* : 19.

Kokal, S. 2005.Crude oil Emulsions: A State of The Art, *SPE, Production & Facilities, Saudi Aramco:* 59.

Kumar, K., A. D. Nikolon, and D. T. Wasan. 2001.Mechanisms of Stabilization of Water-in Crude-Oil Emulsion, *Ind. Eng. Chem. Res*. 40: 3009–3014.

Lemos R. C B., E. A. B. da Silva, A. dos Santos, R. C. L. Guimaraes, B. M. S. Ferreira, R. A. Guarnieri, C. Dariva, E. Franceschi, A. F Santos and M. Fortuny. 2010.Demulsification of Water-in-Crude Oil Emulsions using Ionic liquids and Microwave Irradiation, *Energy Fuels* 24: 4439–4444.

Li J., J. Zhang , H. Yang, Y. Ning.2006.Separation and Characterization of Alkyl Phenol Formaldehyde Resinsdemulsifier by Adsorption Chromatography, Gel Permeation Chromatography، Infrared Spectrometry and Nuclear Magnetic Resonance Spectroscopy, *Analytica Chimica Acta* 566: 224–237

Mohammed S.A.M. and M.S. Mohammed. 2013.The Application of Microwave Technology in Demulsification of Water-in-Oil Emulsion for Missan Oil Fields, *IJCPE* 14(2) :21- 27.

Nguyen T. D..2013.Demulsifier Composition And Method Of Using Same, *US Patent* : 20130261227 A1.

Nour, H., Abdurahman H., M. R. Yunus, and H. Anwaruddin.2006. Water-in-Crude Oil Emulsions: Its Stabilization and Demulsification, *J. Applied Sci*. 7: 19.

Nour H. Abdurahman, A.N. l. Anisa and H. N. Azhari. 2012. Demulsification of Water-in-Oil (W/O) Emulsion via Microwave Irradiation: An Optimization, *Scientific Research and Essays* 7(2): 231-243.

Schmidt, R. 2008.[bmim]$AlCl_4$ Ionic Liquid for Deep Desulfurization of Real Fuel, *Energy Fuels* 22: 1774-1778.

Shi, L. J., B. X. Shen and G. Q Wang, 2008.Removal of Naphthenic Acids from Beijiang Crude Oil by Forming Ionic Liquids, *Energy Fuels* 22: 4177-4181.

Sjoblom J., E. E. Johnsen, A. Westvik , M. H. Ese, J. Djuve, I. H. Auflem and H. Kallevik. 2001. Demulsifiers in the Oil Industry, *In Encyclopedic*

Handbook of Emulsion Technology; Sjo¨blom, J., Ed.; Marcel Dekker: New York, USA : 595-620.

Varadaraj R., D. W. Savage and C. H. Brons.2001.Chemical Demulsifier for Desalting Heavy Crude, US Patent: 6,168,702 B1.

Xia L. X., S. W. Lu, and G. Y. Cao. 2002. Demulsification of Emulsions Exploited by Enhanced Oil Recovery System, *Sep. Sci. Technol.* 37:3407-3420.

Xia L. X., S. W. Lu, & Cao, G. Y., 2004. Stability and Demulsification of Emulsions Stabilized by Asphaltenes or Resins, *J. Colloid Interface Sci.* 271:504-506.