Effect of Ionic Liquid Molecular Weight upon Demulsification Efficiency for Crude Oil Emulsions Using Microwave Heating Technique

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***Abstract* - The main aim of the present work is to detect the effect of molecular weight of three hydrophobic ionic liquids 1-Octyl-3-methylimidazolium trifluoromethanesulfonate OMIMI [TFO]$^-$, 1-Octyl-3-methylimidazolium hexafluorophosphate OMIMI [PF6]$^-$,1-hexyl-3-methylimidazolium hexafluorophosphate HMIMI [PF6]$^-$ upon demulsification of water in oil emulsions. The Microwave technology was used as effective heating method liquids. The results showed the clear relation between the molecular weight of ionic liquids and efficiency of the separation process. The highest separation ratios recorded with the ionic liquid which has the highest molecular weight for all types of crude oil emulsions**

***Index term* - Crude oil demulsification, Ionic liquid, Microwave technology, Molecular weight , W/O emulsions**

I. INTRODUCTION

Modern humanity cannot exist without the consumption of large amounts of energy. Historical progress of the international community was determined by first of all that mankind has managed to use for practical purposes fossils: coal, crude oil and natural gas [1]. So, there are many problems and challenges in the oilfield sector. Some of them are considered very complex and difficult to treat easily. The crude oil emulsion is one of these crucial problems, especially W/O emulsions. Emulsions of crude oil and water can be encountered at many stages during drilling, producing, transporting and processing of crude oils and in many locations such as in hydrocarbon reservoirs, well bores, surface facilities, transportation systems and refineries. In each case, the presence and the nature of emulsion can determine both the economic and technical success of industrial process concerned. A good knowledge of petroleum emulsions is necessary for controlling and improving processes at all stages.

Many studies have been carried out in the last 40 years and have led to a better understanding of these complex systems [2]. The negative effects of W/O emulsion can be summarized depending on the steps of oil production .For the producer, the cost of treating emulsions to reduce the water content of crude oil represents a significant investment in energy , equipments and chemicals. Ideally, the water included as emulsions in crude oil should be resolved as early in the production process as possible (e.g. down-hole) but this requires the ability to introduce the chemicals into the well [3]. While for transporter, the corrosion of pipes are main problems. At the same time, matter is more deep for refinery engineers since the problems have a strong impact because of dissolved salts existence (e.g. NaCl, $MgCl_2$, $CaCl_2$) which contribute in forming corrosive hydrochloric acid leading corrosion of metallic parts of units besides causing fouling and scaling effects. All these problems lead to change the price of crude in international markets [4]-[5]. In addition, oil and gas industry has a negative impact on all components of the environment.

The emulsion breaking (demulsification) process acquired special importance, so the efforts were huge to manufacture strong and effective demulsifiers which most of them had toxic nature. Due to more and more severe environmental constraints, there is now a strong need in the oil production to restrict the use of chemicals and to utilize safer formulations, less toxic but at least as efficient as classical demulsifiers [6]. Many efforts have been performed to develop new strategies for achieving an efficient breaking of W/O emulsions and, consequently, to remove water, salt and solids [7]. One of the methods is to synthesize green demulsifiers. Many formulations were appeared. Some of them were biodegradable ones and others could be recycled. Most prominent examples of green demulsifiers were ionic liquids which began taking an important role in many scientific fields for its special properties. The ionic liquids can be defined that salts which are molten in degree below 100 C especially at room temperature degree. Their low pressure vapor, thermal stability, hydrophilic-hydrophobic characteristics are the most properties of the new materials class [8]-[9]. Besides, new green demulsifiers the scientists tried using microwave irradiation as a new heating method.

The microwave technique is also the promising method because this kind of energy is effective, clean and economic especially it began to substitute the conventional ones in many scientific fields. Mainly, the heating is caused by a dielectric relaxation loss due to rotation of molecules which results from the interaction of the MW electric field with the electric dipole of the molecules. Electric dipoles in liquid or gas experience relatively free rotational motion, comparing with the dipoles in a solid [10]. Especially, the dielectric properties of ionic liquids are made them suitable to use with MW to reach to high and fast separation ratios. Despites, the efforts of scientists for decades to explain the mechanism of demulsification and the factors affected on but still this mechanism is not fully understood [11]-[12] Some of these researches tried to explain the molecular weight effect of different kind of organic demulsifiers on the efficiency of demulsification process [13]-[14]. But for ionic liquids, there are no such studies because of their behavior that is still under the scientific research to understand and to build the basic chemical and physical principles .

So, the molecular weight effect of three hydrophobic imidazolium ionic liquids on demulsification process was investigated in this work.

II. EXPERIMENTAL WORK

2.1 Materials

2.1.1 Crude oil properties

Three types of Iraqi crude oils were used in this work (Nafut Khana (NK), Kirkuk (Kirk), Basrah).The physical and chemical properties are shown in Table 1 as they were obtained from Dura Refinery

Table 1 Physical properties of three types of crude oils

Property	NK	Kirkuk	Basrah
Sp. Gr	0.8095	0.8095	0.8095
API	40	31	26
Asphaltene (%wt)	0.08	1.29	2.1
Sulfur content (% wt)	0.58	0.58	0.58

2.1.2 .Ionic liquids

Three hydrophobic ionic liquids were used (CJC company/ China). All are imidazolium based ionic liquids. They used without any purification. The properties of these materials are listed in Table 2

Table 2 Physical properties of ionic liquids

IL name	M.WT g/gmol	Density g/cm^3	Viscosity cP
HMIM [PF_6]	312.24	1.25	580
OMIM [PF_6]	340.29	1.19	710
OMIMI[TFO]	344.39	1.91	512

2.2 Emulsion preparation

Three crude oils were mixed with saline water (3% wt NaCl). The initial water contents were (8%, 15%, 30%).The emulsification was carried out by using a mixer at a speed of (3000) rpm for (45) minutes to get a stable W/O emulsion. The stability of this emulsion was detected in my previous work and the results showed high stability under these conditions [15].Then the ionic liquids were added (50, 150,300,500) ppm, and mixed for I minute . The emulsion was then heated by using microwave irradiation (Simfer /Turkey) for 50 second and 1000 watts power. After heating, it was left at room temperature for 180 minutes and, the total water removal percentage was recorded as in Eq.1 :

$$\text{SW (\%)} = \frac{separated\ water}{initial\ water\ volume}\ x\ 100 \quad \ldots\ldots(1)$$

Where : SW (100%): final separated water percentage

III. RESULTS & DISCUSSION

3.1 Ionic liquid performance on NK emulsions.

Figures 1, 2, 3 showed the separation efficiency for three ionic liquids with different NK emulsion initial water contents:

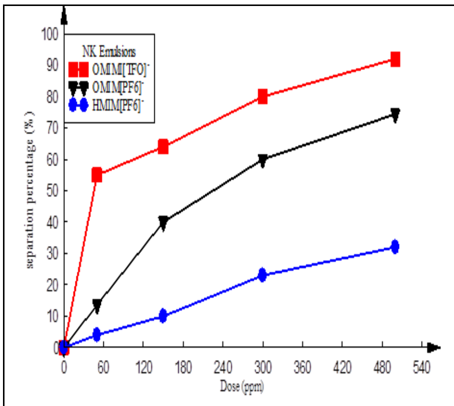

Figure 1 Ionic liquids performance for 8% initial water content of NK emulsion [3% salinity, 1000 watts microwave power, time radiation=50 sec]

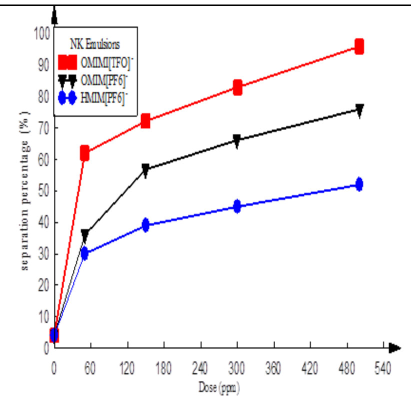

Figure 2 Ionic Liquids performance for 15% initial water content of NK emulsion [3% salinity,1000 watts microwave power ,time radiation=50 sec]

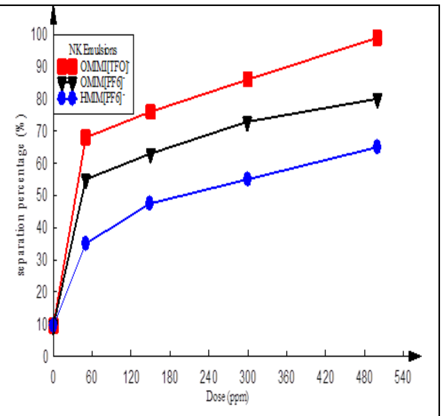

Figure 3 Ionic Liquids performance for 30% initial water content of NK emulsion [3% salinity,1000 watts microwave power ,time radiation=50 sec]

From the figures above, it is noted that the highest separation ratios recorded for OMIMI[TFO].While OMIM[PF6] separation ratios came in second order and the HMIM[PF6] was in third order

3.2 Ionic liquids performance on Kirkuk emulsion

Similar to separation efficiency for NKemulsions, the performance of these compounds was also tested for Kirkuk emulsions. Figures. 4,5 and 6 were clarified the results of this test

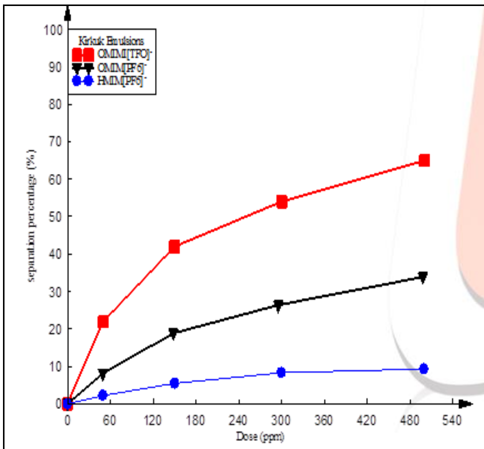

Figure 4 Ionic Liquids performance for 8% initial water content of Kirkuk emulsion [3% salinity, 1000 watts microwave power, time radiation=50 sec]

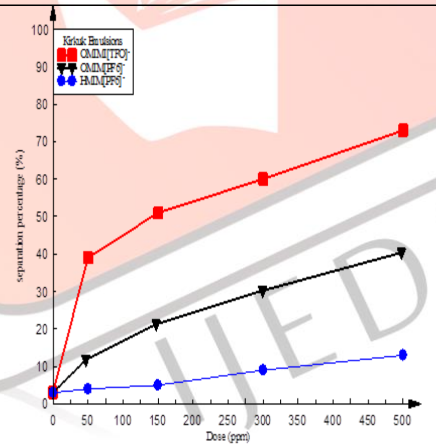

Figure. 5 Ionic Liquids performance for 15% initial water content of Kirkuk emulsion [3% salinity, 1000 watts microwave power, time radiation=50 sec]

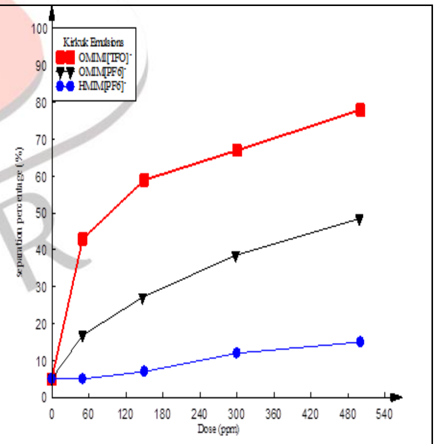

Figure 6 Ionic Liquids performance for30 % initial water content of Kirkuk emulsion [3% salinity, 1000 watts microwave power, time radiation=50 sec]

3.3 Ionic liquids performance on Basrah emulsions

Figures 7,8 and 9 showed the separation percentages for Basrah emulsions

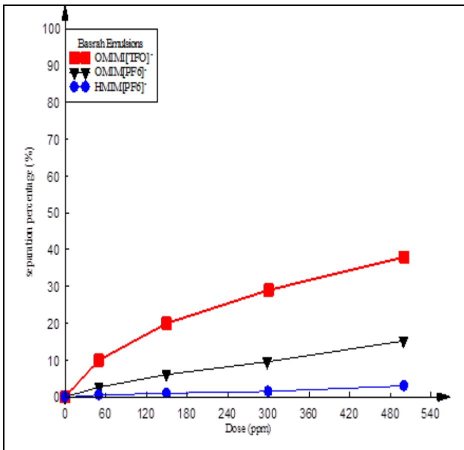

Fig. 7 Ionic Liquids performance for 8 % initial water content of Basrah emulsion [3% salinity, 1000 watts microwave power, time radiation=50 sec]

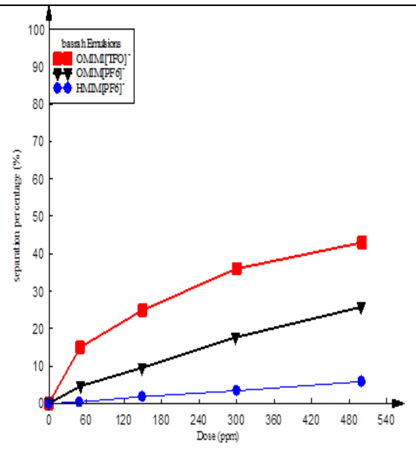

Fig. 8 Ionic Liquids performance for 15 % initial water content of Basrah emulsion[3% salinity, 1000 watts microwave power, time radiation =50 sec]

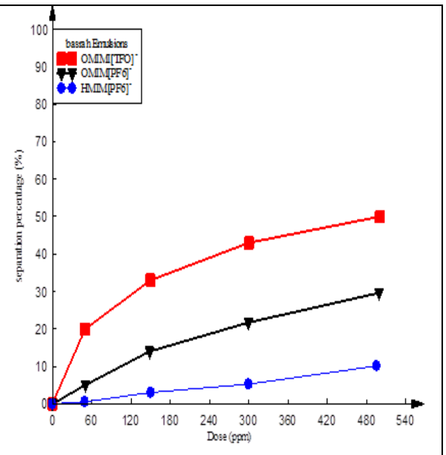

Fig. 9 Ionic Liquids performance for 30 % initial water content of Basrah emulsion[3% salinity, 1000 watts microwave power, time radiation= 50 sec]

It is noted that the separation efficiency increased when doses are increased because of demulsifier molecules perform a complete coverage of the water/oil interface, dragging the asphaltenes away from the interface. As a result, the protecting film present around the dispersed water droplets thins, then it ruptures and coalescence eventuates. Table 3 summarized the final and highest obtained separation ratios of all types of ionic liquids when 500 ppm dose was used

Table 3 The highest separation percentage (500 ppm) of three ionic liquids

Initial water content %	NK Emulsions			Kirkuk Emulsions			Basrah Emulsion		
	OMIMI [TFO] %	OMIM $[PF_6]$ %	HMIM $[PF_6]$ %	OMIMI [TFO] %	OMIM $[PF_6]$ %	HMIM $[PF_6]$ %	OMIMI [TFO] %	OMIM $[PF_6]$ %	HMIM $[PF_6]$ %
30%	99	85	65	78	49	15	50	30	11
15%	96	76	52	73	40	13	43	25	6
8%	92	70	32	65	34	9	38	15	3

Depending on the results of curves and table which are listed above, the clear conclusion is that OMIMI $[TFO]^-$ which holds the highest molecular weight has the highest water separation ratios in all cases and with different crude oil types and different initial contents. While OMIM [PF6] results come in second order, whereas HMIM [PF6] performance, which holds the lowest molecular weight, has the lowest results. This can be explained, depending on the fact that the properties of the ILs can significantly change by varying the length of the alkyl groups that are incorporated into the cation and the types of anions .

So, the first reason is attributed to alkyl chain length because the increase of molecular weight is a result of the increasing in chain length. It is a clear from the structure of ionic liquids where the ionic liquids are special classes of surfactants consist of cations and anions. So the chain length plays a dramatic role in the performance of them. The alkyl chain length has effect on the physical, chemical properties and the intermolecular forces which play an important role in emulsion stability. The increase in extraction efficiency for ILs as the length of the alkyl chain attached to the cation. Varying the length of the alkyl group has an effective role on the physical properties, especially hydrophobicity and molecular weight of ionic liquids that contribute to improve the demulsification performance.

The other reason of these results is the structure,type and length of an ion. OMIMI [TFO] and OMIM [PF6] have the same alkyl chain (Octyl) but they differ in anion structure which leads to make molecular weight of OMIMI [TFO] higher than OMIM [PF6]. The anion [TFO] is more effective than [PF6].The anion specifies the hydrophilicity and hydrophobicity of ionic liquids. To demulsify W/O emulsion , it needs ionic liquids with hydrophobic characteristics which have ability to be soluble in oils in order to reach to the interfacial film quickly to react or to interact with asphaltene and other materials in that film to make coalescence of water droplets easier. On the contrary, the ionic liquids with hydrophilic anion needs more time and high dose to overcome the difficulties which are existed in the continuous phase (oil) because of its low solubility. The anions tested in this research can be classified according to increased hydrophobicity in the following order PF6< trifluoromethansulfonate. The results of demulsification efficiency varied according to the hydrophobicity of the two anions. The trifluoromethansulfonate, which is used in this work for the first time as crude oil emulsion demulsifier, was the more efficient than PF6. The anion effect of ionic liquid subjected to deep research in recent years.

Besides, the differences in separation efficiency between three types of crude oils can be attributed to chemical structure of oils themselves especially the asphaltenes ratio which is varied from low to high ratio. NK crude oil has the lowest ratio while Kirkuk crude oil comes in second order but the high ratio of asphaltenes is for Basrah crude oil.

VI. CONCLUSION

Depending on the results of the present study, the molecular weight of the hydrophobic ionic liquids has important role on the separation performance of these materials .The highest separation ratios recorded for OMIMI[TFO] , OMIM [PF6] and HMIM [PF6] respectively for all crude oil types and different initial water content contents . The molecular weight increase is a result of alkyl chain increase and anion structure.

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