JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

ARTICLE

pubs.acs.org/jced

Effect of a Different Formulation of Demulsifiers on the Efficiency of Chemical Demulsification of Heavy Crude Oil

Maryam Razi, Mohammad Reza Rahimpour,* Abdolhossein Jahanmiri, and Farshad Azad

Department of Chemical Engineering, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz 71345, Iran

ABSTRACT: The stability of water-in-oil emulsions formed during oil slicks or petroleum production operations is ensured by natural surfactant molecules (principally asphaltenes) that are present in the crude oil. These persistent emulsions may be broken by adding a suitable demulsifier at the proper concentration to attain a so-called optimum formulation at which the emulsion has the minimum stability. In this work, a new formulation for demulsifier has been developed which is more suitable for demulsification of heavy crude oil than the other formulations which are used nowadays. The factors affecting the demulsification are discussed, and the final formulation regardless of its price is achieved. The results confirm that the best single demulsifiers are those which cause a minimum in the interfacial tension of water and heavy crude oil. Composite demulsifier screening was used to analyze the best mixture of single demulsifiers which possess the best efficiency at water separation from heavy crude oil.

INTRODUCTION

Emulsified water is generally present in crude oil as a result of the mixing occurring during production operations. Because it adds up to the cost of petroleum transportation and refining, water must be separated, and since the emulsion aging tends to increase its stability, the breaking must be carried out as soon as possible in the production facility close to the well. These water/oil (W/O) type emulsions are mostly stabilized by naturally occurring surfactants, for example, asphaltenes, resins, and waxes which adsorb at interfaces and tend to inhibit or delay the interdrop film drainage, hence preventing drop—drop coalescence and water separation.[1] Several approaches have been reported to study the associated phenomena, and some trends and correlations have been found between properties.[2−9] However, the general phenomenology is not completely understood, certainly because there are (too) many concomitant effects in extremely complex systems from the chemical point of view, so that direct and clear-cut analysis is essentially impossible. Natural surfactants are referred to as asphaltenes in the present paper because these species have been shown to play the major role in stabilizing the emulsion. Asphaltenes correspond to the fraction of the crude oil that is insoluble in an excess of low-molecular-weight alkanes, usually pentane or heptane, but which is soluble in methylbenzene. Recent studies consider that asphaltenes have a molar mass between (0.4 and 1.5) $kg \cdot mol^{-1}$. They usually exhibit a condensed matrix containing aromatic rings associated with heteroatoms, which result in some polarity, and some alkyl chains that provide a good match with the maltene a polar fraction. Because of their polar groups, asphaltenes are surfactants that tend to adsorb at the interface and stabilize W/O emulsions. Figure 1 represents the range of heavy compounds precipitated by mixing crude oil with pentane and heptane.

The resins are defined as the nonvolatile and polar fraction of crude oil that is soluble in pentane, heptane, and aromatic solvents such as methylbenzene but insoluble in propan-2-ol. The molecular species within the resin are same as to those in the aromatics. But, resin species have a higher molar mass, greater polarity, higher heteroatom content, and lower H/C ratio compared to aromatics. The resin fraction consists of carbon, hydrogen, oxygen, nitrogen, and naphthenic acids. Resins have a much higher H/C ratio compared to asphaltenes, indicating that they are less aromatic than asphaltenes. Asphaltenes are presumed to be maturation products of resin; in the maturation process the cyclic portion of resin molecules undergoes aromatization.

Waxes are high molecular weight alkanes. A sensible description of wax is anything with a waxy feel and a melting point above body temperature and below the boiling point of water. Waxes have been defined as esters of long-chain (C_{16} and above), monohydric (one hydroxyl group), or alcohols with long-chain (C_{16} and above) fatty acids. Actually, the natural waxes are mixtures of esters and frequently contain hydrocarbon as well. Majority of the waxes present in crude oil are in the form of monoxidized alkanes. This is because of the anaerobic conditions under which biodegradation of organic matter takes place to form crude oils. Wax molecules can combine with the fatty tails of the carboxylic acids stabilizing the interface.[10] Methods to induce phase separation in water-in-crude oil emulsions can be classified in three main categories: mechanical, electrical, and chemical. Chemical demulsification consists of the addition of minute amounts of chemical compounds (usually 10^{-5} to 10^{-3} mass fraction) to enhance phase separation rates. It is the most economical and commonly used method of dehydration of crude oils. A combination of chemical and mechanical or chemical and electrical is often the best choice for practical applications. Each component plays a specific role in the performance of a modern demulsifying formulation. Amphiphilic molecules with moderate-to-high molar mass (typically above 3 $kg \cdot mol^{-1}$), such as polyalkoxylated alkylphenol formaldehyde resins and complex block copolymers, are usually responsible for the separation of a

Received: February 18, 2011
Accepted: April 27, 2011
Published: May 10, 2011

dx.doi.org/10.1021/je2001733 | *J. Chem. Eng. Data* 2011, 56, 2936–2945

large fraction of the dispersed aqueous phase. For that reason, they are often termed water droppers.

Several studies suggest that these molecules act by modifying the compressibility[11,12] and rheological properties[13,14] of the water−oil interfacial films that stabilize the emulsion in a way that favors the drainage of the thin films between approaching drops and therefore coalescence and phase separation. Molecules with very high molar mass (usually above 10 $\text{kg} \cdot \text{mol}^{-1}$) such as ethoxylated-propoxylated amine polyols act as flocculants by adsorbing at the water−oil interfaces and interacting with like molecules also adsorbed at the interfaces of nearby drops. These molecules act more slowly due to their lower diffusivities and are effective in removing remaining small water drops and tight, fine emulsions once most of the dispersed phase has been removed by the water droppers. Low molar mass compounds (typically below 3 $\text{kg} \cdot \text{mol}^{-1}$), such as common surfactants, exhibit high interfacial activity and diffuse faster than other components with higher molecular weight. Therefore, they can suppress more effectively the interfacial tension gradients that occur in deforming interfaces of approaching drops, which otherwise would retard drainage of the corresponding thin films that precede film rupture and coalescence.

Solvents are used as carriers of the active molecules, and they can play a critical role in the performance of a demulsifying formula. Aromatic hydrocarbons such as methylbenzene and 1,4-dimethylbenzene and heavy aromatic naphtha, water-miscible hydroxy compounds such as butan-1-ol, propan-2-ol, and ethane-1,2-diols are often used as solvents in the formulation of commercial demulsifiers. The solvent must be chosen to minimize the size of the aggregates that these active molecules may form in solution, so they can be dispersed readily once dosed to the emulsion. A poor selection of solvent may result in a delay in the rate of phase separation and therefore in an increase in the concentration of demulsifier needed to resolve the emulsion in a practical time frame.

Few studies are found in the literature reporting the effect of systematic changes in the chemistry of demulsifiers on their performance, probably because such information is often left unpublished for commercial reasons or is patent-protected.[15]

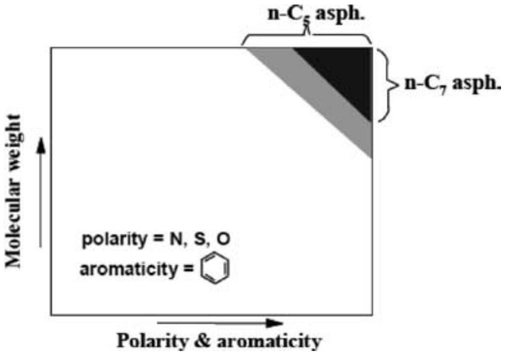

Figure 1. Hypothetical diagram representing the molecular characteristics of the asphaltenes precipitated from petroleum by n-alkane addition.

The objective of this study is to identify and screen the existing demulsifiers and create the new demulsifier formulation for the demulsification of heavy crude oil emulsion.

First, the study will be focused on a single demulsifier in both water and oil-soluble groups. This test will be carried out by using the bottle test method at the fixed concentration and temperature for real emulsion systems (medium and heavy crude oil).

Second, by using the best demulsifiers from both groups, the test will be proceeding by varying the concentration to know the flow pattern of demulsification and concentration.

The results of these studies will lead to the combination of demulsifiers.

Finally, the effectiveness of this formulation will be tested by using single emulsion system and will be compared with other commercial demulsifiers formulation. The excellent result will be measured from the water separation level.

Influence of the Formulation on Emulsion Stability. It is generally easy to state that an emulsion is broken, but it is often difficult to give a numerical estimate of the stability of an emulsion that is not completely resolved. The stability, which is actually rather the persistence because an emulsion is not thermodynamically stable, may be estimated (for comparison purposes) by measuring the volume of separated phases with time. This criterion is often used satisfactorily to compare emulsions having different separation rates.[16,17]

The plot of the separated volume fraction versus time often exhibits a sigmoid shape, characteristic of a three-step process. First, the long distance approach of drops because of gravitational sedimentation (or other body force, such as electrostatic attraction) results in a compacted emulsion in which the drops are separated by thin films of external phase. This first step depends upon physical parameters, such as drop size, density difference, and external phase viscosity. Then, the second step is the drainage of the thin film, which depends upon the protective effect of the surfactant adsorbed at approaching interfaces. The surfactant performance essentially depends upon the physicochemical formulation, that is, the nature of the different components, as well as temperature and pressure. If the film drains, it finally becomes so thin that it breaks, resulting in the third step, which is the coalescence of drops that produces the phase separation. Because the last step is essentially instantaneous, it may be said that the limiting step is generally the second one,

Table 1. Characterization of Crude Oils

	medium oil	heavy oil
mass density/$\text{kg} \cdot \text{m}^{-3}$ at 15 °C	868	1006
viscosity/$\text{mPa} \cdot \text{s}$ at 15 °C	21.7	29.95
salt content of produced water/$\text{kg} \cdot \text{m}^{-3}$	205	17
mass fraction of wax	0.078	0.064
mass fraction of water	0.0442	0.1838
mass fraction of saturates	0.45	0.322
mass fraction of aromatics	0.32	0.464
mass fraction of resins	0.08	0.135
mass fraction of asphaltenes	0.05	0.068

Table 2. Chemical Composition of Crude Oils

component	C_1	C_2	C_3	IC_4	NC_4	IC_5	NC_5	C_6	C_7^+	H_2S	CO_2	N_2
mole fraction in medium oil	0.0021	0.0042	0.0270	0.0109	0.0380	0.0224	0.0303	0.0548	0.8095	0.0005	0.0003	0.0000
mole fraction in heavy oil	0.3718	0.0990	0.0610	0.0126	0.0338	0.0119	0.0128	0.0461	0.3430	0.0000	0.0053	0.0027

Table 3. Materials Used as a Demulsifier for the Demulsification of Medium and Heavy Crude Oil

no.	name	purity/mass fraction	supplier
1	methyl 2-methylpropenoate (methyl methacrylate, MMC)	>0.99	Sigma-Aldrich
2	butyl-2-propenoate (butyl acrylate, BA)	>0.99	Merck Chemical
3	2-methylpropenoic acid (methacrylic acid, MCA)	>0.99	Merck Chemical
4	sodium dodecyl sulfate (SDS)	>0.85	Merck Chemical
5	2-ethylhexyl prop-2-enoate (2-ethylhexyl acrylate, 2-EHA)	>0.99	Merck Chemical
6	1-ethenylpyrrolidin-2-one (polyvinylpyrrolidone, PVP)	>0.90	Merck Chemical
7	hexan-1-amine (hexylamine, HA)	>0.99	Sigma-Aldrich
8	methyl(trioctyl)azanium chloride (methyl trioctyl ammonium chloride, TOMAC)	>0.90	Merck Chemical
9	furan-2,5-dione (maleic anhydride, MA)	>0.99	Merck Chemical
10	2-[4,5-diethoxy-2-(ethoxymethyl)-6-methoxy-oxan-3-yl]oxy-6-(hydroxymethyl)-5-methoxy-oxane-3,4-diol (ethylcellulose polymer, EC)	>0.90	Sigma-Aldrich
11	CO-720 (IGEPAL Series)	>0.999	Sigma-Aldrich
12	CA-720 (IGEPAL Series)	>0.999	Sigma-Aldrich
13	KENON 10	>0.99	Kimyagaran Emrooz Co., Iran
14	KENON 20	>0.99	Kimyagaran Emrooz Co., Iran
15	silicone surfactant (SS)	>0.99	Supreme Silicones Co., India
16	oxirane/epoxypropane block copolymer (EO/PO block copolymer)	>0.99	Venus Ethoxylated Co., India
17	alkoxylated alkyl phenol formaldehyde resin (NPFE)		synthesized
18	V-4654[a]		Hallal Shimi Pars Co., Iran
19	RP-6348[a]		Pars Lyan Co., Iran

[a] Commercial formulation.

Table 4. Chemical Composition of Materials Used as a Demulsifier for the Demulsification of Medium and Heavy Crude Oil

no.	name	chemical composition/mass fraction
1	MMC	C, 0.5998; H, 0.0805; O, 0.3196
2	BA	C, 0.6560; H, 0.0944; O, 0.2497
3	MCA	C, 0.5581; H, 0.0702; O, 0.3717
4	SDS	C, 0.4998; H, 0.0874; Na, 0.0797; O, 0.2219; S, 0.1112
5	2-EHA	C, 0.7170; H, 0.1094; O, 0.1736
6	PVP	C, 0.6484; H, 0.0816; N, 0.1260; O, 0.1440
7	HA	C, 0.7122; H, 0.1494; N, 0.1384
8	TOMAC	C, 0.7429; H, 0.1347; Cl, 0.0877; N, 0.0347
9	MA	C, 0.4899; H, 0.0206; O, 0.4895
10	EC	C, 0.5852; H, 0.0901; O, 0.3247
11	CO-720	C, 0.8719; H, 0.0331; O, 0.0950
12	CA-720	C, 0.5812; H, 0.0550; O, 0.3638
13	KENON 10	C, 0.4514; H, 0.0674; O, 0.4812
14	KENON 20	C, 0.5519; H, 0.0850; O, 0.3631
15	SS	C, 0.4703; H, 0.0989; O, 0.1566; Si, 0.2742
16	EO/PO block copolymer	C, 0.5878; H, 0.0989; O, 0.3133
17	NPFE	C, 0.7341; H, 0.1029; O, 0.1630
18	V-4654[a]	C, 0.6562; H, 0.2238; O, 0.1200
19	RP-6348[a]	C, 0.5954; H, 0.1537; O, 0.1940; N, 0.0569

[a] Commercial formulation.

which involves the physicochemical formulation. As a way to quantify the effect of formulation, the stability is often taken as the time required for the separation of 1/2 (or another fraction) of the internal phase.

Crude Oil Characterization. Crude oils used for these sets of experiments are from two oil fields, Gachsaran medium crude and Cheshmeh-khosh heavy crude oil. Their physical characteristics are shown in Table 1. The crude oil chemical composition is shown in Table 2.

■ EXPERIMENTAL SECTION

Materials and Equipment. There are wide ranges of demulsifiers that can be used in the demulsification of crude oil emulsions. The surfactant demulsifiers used in this study are shown in Table 3. Their chemical composition is depicted in Table 4. Some demulsifiers were from Sigma-Aldrich or Merck Company. The other materials were from Supreme Silicones, Venus Ethoxylated, and Kimyagaran Emrooz Company. All solvents and cosolvents used in these experiments are shown in Table 5. The syringes used for the experiments were Hamilton micro syringes. The shaker was a IKA KS 130 basic. The incubator was of Friocell type.

Preparation of Stable Emulsions. To prepare the stable emulsion, water containing the surfactant at the corresponding concentration was added to each crude oil sample (medium, heavy) preheated to 70 °C to obtain a water content of 20 % (wt) in each case, taking into account the original water content in each crude oil used in this study. The emulsions were prepared by mixing in a shaker at 800 rpm for 15 min. A stable W/O emulsion was thus obtained. The emulsions prepared in this way were stable for weeks without apparent phase separation.

Demulsification Tests. Each individual and complex surfactant were evaluated as the demulsifier using the probe known as the bottle test according to the following procedure.[18]

Bottle Test. The emulsions formed according to the procedure described above were transferred to graduated glass bottles (100 mL). The test was carried out using 100 mL of crude oil in each case in the incubator at a constant temperature (70 °C). An amount value of demulsifier was added to the emulsion using the micro syringe to obtain a content of 10^{-4} mass fraction of additive, and then the bottles were stopped and shaken for 5 min to thoroughly mix the demulsifier and the emulsion. The bottles were then returned to the incubator, and the separation of phases was monitored by the position of the oil/emulsion interface and recorded as a function of time to obtain the volume of water separated every 5 min. A bottle containing a crude oil sample and water without any additives was employed as a reference (blank). The relative errors in the estimation of the volume of the resolved oil phase are 5 % for low-resolution tests (1 mL of oil or 15 % separation) to less than 1 % for high resolution tests (>5 mL of oil or >70 % separation). The performance of the demulsifiers was measured in terms of percent volume of water separated (WS), vol %, which is defined as

$$\text{water separation}(v/v\%) = v/v^0 \cdot 100 \tag{1}$$

where v is the volume of the water separated and v^0 is the original volume of water contained.

Table 5. Solvents and Cosolvents Used as Assistants for Demulsifier in the Demulsification of Heavy Crude Oil

no.	name	purity/mass fraction	oil or water solubility
1	methylbenzene	>0.99	oil soluble solvent
2	1,4-dimethylbenzene	>0.99	oil soluble solvent
3	heavy aromatic naphtha	>0.99	oil soluble solvent
4	butan-1-ol	>0.99	water-soluble solvent
5	propan-2-ol	>0.99	water-soluble solvent
6	propanone	>0.99	water-soluble solvent

■ RESULTS AND DISCUSSION

Effect of Different Water-Soluble Surfactant Demulsifiers on the Demulsification of Medium Crude Oil. As seen in Figure 2, different surfactant demulsifiers have a different water separation efficiency. In this figure, it is obvious that butyl-2-propenoate (BA), methyl 2-methylpropenoate (MMC), and sodium dodecyl sulfate (SDS) have the best efficiencies, respectively. It is worth mentioning that about 80 volume percent of water is separated during the primitive minutes of experiment and the remainder is separated a long time after the initiation of the experiment. The efficiency of surfactants to act as a demulsifier is much better for medium crude oil than their efficiency for demulsification of heavy crude oil as will have seen later in Figure 3. This may be due to the lower asphaltene content of medium crude oil relative to heavy crude oil. As was proven before, asphaltenes are one of the key factors to stabilize the crude oil emulsions. The dosage of demulsifier injection to the emulsion is $2 \cdot 10^{-4}$ mass fraction, and the operating temperature is 70 °C.

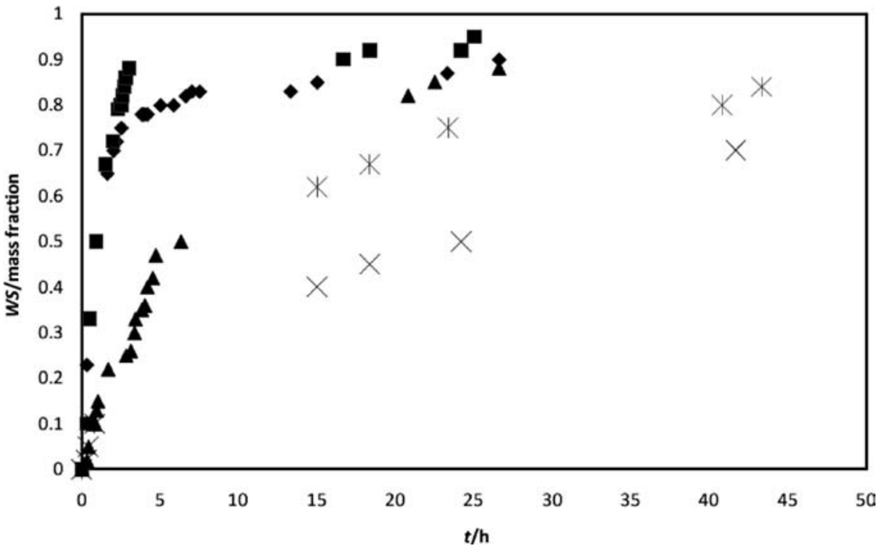

Figure 2. Effect of different water-soluble surfactant demulsifiers on demulsification of medium crude oil during time. WS stands for water separation. Results: ♦, MMC; ■, BA; ▲, SDS; ×, MCA; ∗, 2-EHA.

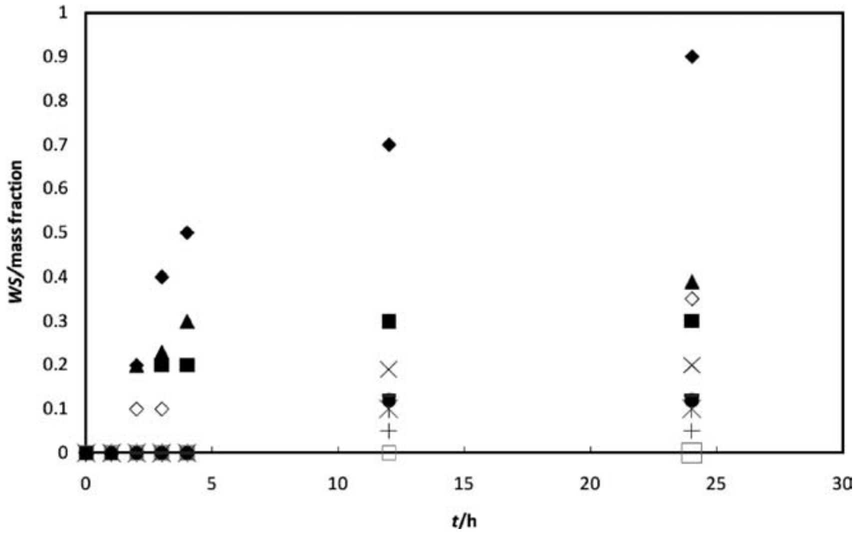

Figure 3. Effect of different water-soluble and oil soluble surfactant demulsifiers on the demulsification of heavy crude oil during time: ◇, MMC; ■, BA; ▲, SDS; ×, MCA; ∗, 2-EHA; ●, PVP; +, HA; □, MA; −, TOMAC; ◆, V-4654.

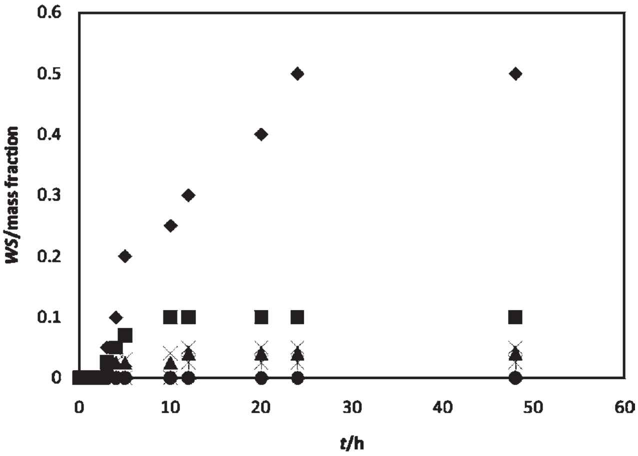

Figure 4. Effect of different surfactant demulsifiers on the demulsification of heavy crude oil during time: ◆, TOMAC; ■, EC; ▲, CO-720; ×, CA-720; ∗, KENON10; ●, KENON20.

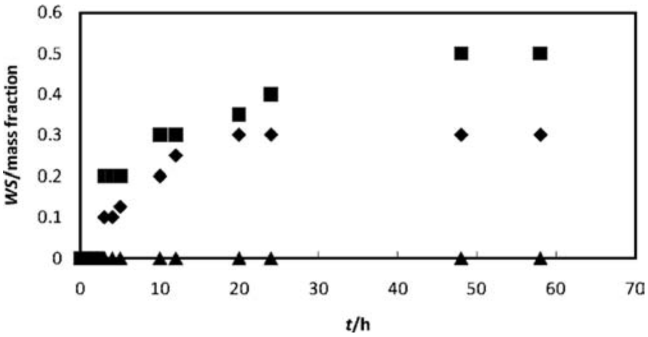

Figure 5. Effect of different surfactant demulsifiers on the demulsification of heavy crude oil during time: ◆, SS; ■, EO/PO block copolymer; ▲, blank.

Effect of Different Water-Soluble and Oil Soluble Surfactant Demulsifiers on the Demulsification of Heavy Crude Oil. As seen in Figure 3, single demulsifiers have low efficiency to act as demulsifier for treatment of heavy crude oil. In this case they should be mixed with other active ingredients to improve their efficiency as emulsion breakers. As seen in this figure water-soluble surfactant demulsifiers show better performance as demulsifiers. V-4654 is a commercial demulsifier which is used commonly in Iran for the demulsification of heavy crude oil. The surfactant injection dosage in this test is $2 \cdot 10^{-4}$ mass fraction, and the operating temperature is 70 °C.

Figure 4 illustrates the efficiency of different new demulsifiers for demulsification of heavy crude oil. The dosage of demulsifier injection in this test is 10^{-3} mass fraction, and the operating temperature is 70 °C. Methyl trioctyl azanium chloride (TOMAC) was purchased from Merck Chemicals and was used as received.

The commercial nonionic surfactants polyethoxylated 4-(2,4-dimethylheptan-3-yl)phenol (polyethoxylated nonylphenols; CO-720, CA-720; $C_9H_{19}C_6H_4(OC_2H_4)_nOH$) are Igepal series from Aldrich. They are polydispersed mixtures whose degree of ethoxylation is distributed according to Poisson's law. Their hydrophobic nonyl chains are believed to have a branched structure that results from the polymerization of propylene. Their efficiency as emulsion inhibitors and demulsifiers was proven before by the work of Fan et al.[19]

Heavy aromatic naphtha was supplied by Hydrocarbon Iran Co. HPLC-grade methylbenzene and propanone were purchased from Fisher Scientific. 2-[4,5-Diethoxy-2-(ethoxymethyl)-6-methoxy-oxan-3-yl]oxy-6-(hydroxymethyl)-5-methoxy-oxane-3,4-diol (EC) with 48 % ethoxyl was purchased from Sigma-Aldrich and used as received. The molar mass of the polymer was determined by intrinsic viscosity measurement to be 46 $\text{kg} \cdot \text{mol}^{-1}$. EC was dissolved in heavy naphtha and stirred for 24 h prior to its use.

KENON 10 and KENON 20 are nonyl phenol ethoxylates provided by Kimyagaran Emrooz Co., Iran with the ethoxyl content of (10 and 20) %, respectively. As seen in this figure TOMAC possesses the best efficiency among these groups of demulsifiers, and its water separation efficiency reaches to 50 % along 24 h of experiment.

As seen in Figure 5, the effect of different demulsifiers on crude oil demulsification efficiency is different. Oxirane/epoxypropane block copolymer (EO/PO block copolymer) was purchased from Venus Ethoxylated Co., India and used as received. Silicone surfactant (SS) was purchased from Supreme Silicones Co., India. The silicone surfactant characteristics are shown in Table 6. As seen in Figure 5, the EO/PO block copolymer has the best rate of water removal from the crude oil emulsion compared to SS individually. To the best of our knowledge it is the first time that efficiency of different demulsifiers is compared to formulate a new demulsifier to apply for demulsification of heavy crude oil. A blank sample is tested to show the rate of water separation without adding any demulsifier.

Figure 6 depicts the efficiency of different ethoxylation number of ethoxylated nonylphenol formaldehyde resin (NPFE) for emulsion breaking of heavy crude oil. Table 7 shows the different content of oxirane in resin.

As seen in Figure 6, sample number 3 shows the best efficiency during all samples. It is worth to mention that V-4654 is a commercial demulsifier which is a blend of different surfactants, cosurfactants, wetting agents, flocculating agents, and coalescers. In this research it is important to monitor the effect of single demulsifiers in the demulsification of heavy crude oil regardless of its price.

It was rather known that the best efficiency of sample 3 is because of its moderate affinity to oil and water phases. As was proven before, demulsifiers with moderate water solubility and oil solubility with partition coefficient close to unity are more efficient at water separation of crude oil emulsions than those with high oil solubility and low water solubility.[20]

The effect of composite demulsifiers on the destabilization of heavy crude oil emulsions is illustrated in Figure 7. Notice that, in this case, the oil phase is a heavy crude oil which has a relatively high (approximately 30 mPa·s @ 15 °C) bulk viscosity. As seen in this figure, a combination of EO/PO block copolymer, TOMAC and NPFE possesses the best efficiency among all other combinations in this test. In this case water separation efficiency reaches to 80 % during 150 min of the experiment.

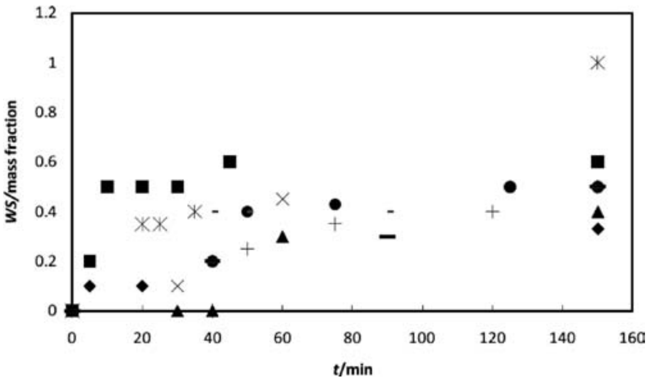

Figure 6. Effect of different ethoxylation content of NPFE on the demulsification of heavy crude oil during time: ♦, 2; ■, 3; ▲, 4; ×, 5; ∗, V-4654; ●, 7; +, 8; -, 9; −, 10.

The demulsification performance of new composite demulsifier is shown in Figure 8. As seen in this figure, the water separated from emulsion has relative clearance.

Having a sharp interface between oil and water phase is another criterion to formulate a new demulsifier composite. Figure 9 illustrates the demulsification efficiency of commercial demulsifier V-4654 for treating heavy crude oil of Cheshmeh Khosh field of Iran. As seen in this figure, there is no sharp interface between the oil and the water phases, and the water separated from demulsificated crude oil in this figure is rather unclear.

Crude Oil/Brine Dynamic Interfacial Tensions. Interfacial tension (IFT) values between crude oil and aqueous solutions are time-dependent. This may be due to slow diffusion of some components across the interface, although changes with time are not eliminated by pre-equilibration of the oleic and aqueous phases.[21]

Because crude oil/brine IFT is time-dependent, different values can be found by different techniques. As the oil phase, a 33.73/66.27 mass fraction of methylbenzene/decane blend was used and as the water phase, a 3.5 % NaCl solution. The demulsifiers were added at 100 mass ppm concentration into the water phase. The IFT was measured using a pendant drop tensiometer from Kruss at 25 °C. To characterize the dynamics of the adsorption the IFT was measured every 60 s.

As seen in Figure 10a the sample without any demulsifier does not meet any noticeable reduction in interfacial tension during the time; some surfactants like furan-2,5-dione (MA) and 1-ethenylpyrrolidin-2-one (PVP) do not change the interfacial tension too much, and their initial interfacial tension is to some extent high. As seen in this figure, the surfactants like MMC, hexan-1-amine (HA), and 2-ethylhexyl prop-2-enoate (2-EHA) possess the highest reduction in interfacial tension. Low interfacial tension is not the only parameter that can affect the demulsification of crude oil but can be considered as a necessary condition for it (as long as the demulsifier is not a treater). The low interfacial tension can be one of the important factors for coalescence of water drops in water-in-crude oil emulsions.

Figure 10b illustrates the dynamics of interfacial tension during 600 s. As seen in this figure, the surfactant demulsifier named as CO-720 has the most reduction in interfacial tension among this group of surfactant demulsifiers.

Dynamic interfacial tensions of SS and EO/PO block copolymer are shown in Figure 10c. As seen in this figure, the EO/PO block copolymer has the lowest interfacial tension and thus has a good compatibility with the bottle test results (Figure 5).

Dynamic interfacial tensions of NPFE and commercial demulsifier formulations, V-4654 and RP-6348, are depicted in Figure 10d. As seen in this figure, NPFE and commercial demulsifier formulations have relatively low interfacial tensions. These results show that the water separation rate could be proportional to the reduction of interfacial tension by a surfactant demulsifier during time.

Table 6. SS Characteristics

silicone surfactant	RSN (relative solubility number)	kinematic viscosity	flash point	mass density	molar mass	cloud point
		$m^2 \cdot s^{-1}$ @ 20 °C	°C	$kg \cdot m^{-3}$ @ 20 °C	$kg \cdot mol^{-1}$	°C
	14.2	0.00048	115	1030	medium	60

Table 7. Ethoxylation Content of Different Samples of NPFE

sample no.	ethylene oxide (EO)/mass fraction	EO/nonyl phenol formaldehyde resin/mass fraction
2	0.2837	0.3962
3	0.3333	0.5000
4	0.3750	0.6000
5	0.3981	0.6615
7	0.4444	0.8000
8	0.4583	0.8462
9	0.4715	0.8923
10	0.4800	0.9231

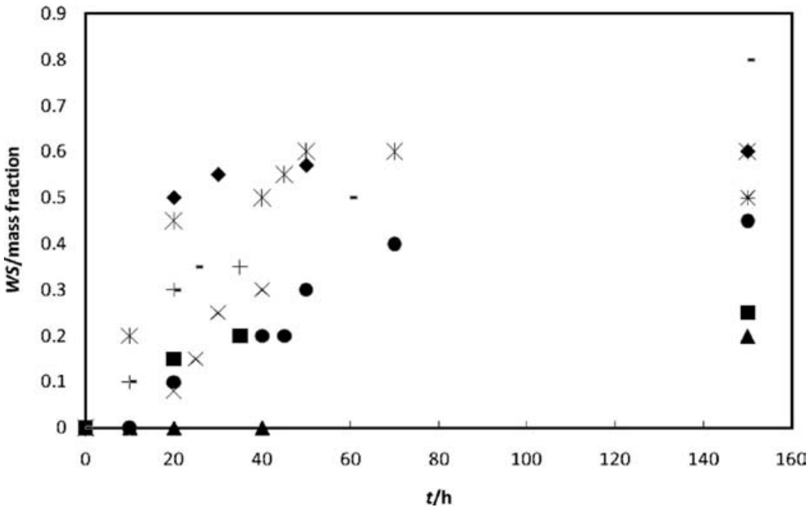

Figure 7. Effect of different mixtures of surfactant on the demulsification of heavy crude oil. Quantities are expressed in terms of mass fraction: ♦, $3\cdot10^{-4}$ EO/PO block copolymer + $3\cdot10^{-4}$ NPFE3; ■, $3\cdot10^{-4}$ EO/PO block copolymer + $3\cdot10^{-4}$ NPFE2; ▲, 10^{-3} TOMAC + $4\cdot10^{-4}$ SS + $3\cdot10^{-4}$ EO/PO block copolymer + $3\cdot10^{-4}$ NPFE3; ×, 10^{-3} TOMAC + $3\cdot10^{-4}$ NPFE5 + $3\cdot10^{-4}$ EO/PO block copolymer; ∗, $2\cdot10^{-4}$ TOMAC + $3\cdot10^{-4}$ NPFE3 + $2\cdot10^{-4}$ EO/PO block copolymer; ●, $2\cdot10^{-4}$ SS + $3\cdot10^{-4}$ NPFE5 + $3\cdot10^{-4}$ EO/PO block copolymer; +, $2\cdot10^{-4}$ TOMAC+ $3\cdot10^{-4}$ NPFE5 + $2\cdot10^{-4}$ EO/PO block copolymer; −, $2\cdot10^{-4}$ TOMAC + $2\cdot10^{-4}$ NPFE3 concentrated + $2\cdot10^{-4}$ EO/PO block copolymer.

Figure 8. Demulsification results for the heavy crude oil emulsion after 2.5 h at 70 °C with a new composite demulsifier.

Figure 9. Demulsification results for the heavy crude oil emulsion after 2.5 h at 70 °C with a commercial demulsifier.

Figure 11 depicts the bottle test results for several formulations of chemical demulsifiers. The two bottles from the left in the picture are the crude oil emulsions without adding any demulsifiers. The third bottle from the left shows the crude oil emulsion treated by adding the new formulation, and the last one from the left is the crude oil emulsion with commercial formulation. It is

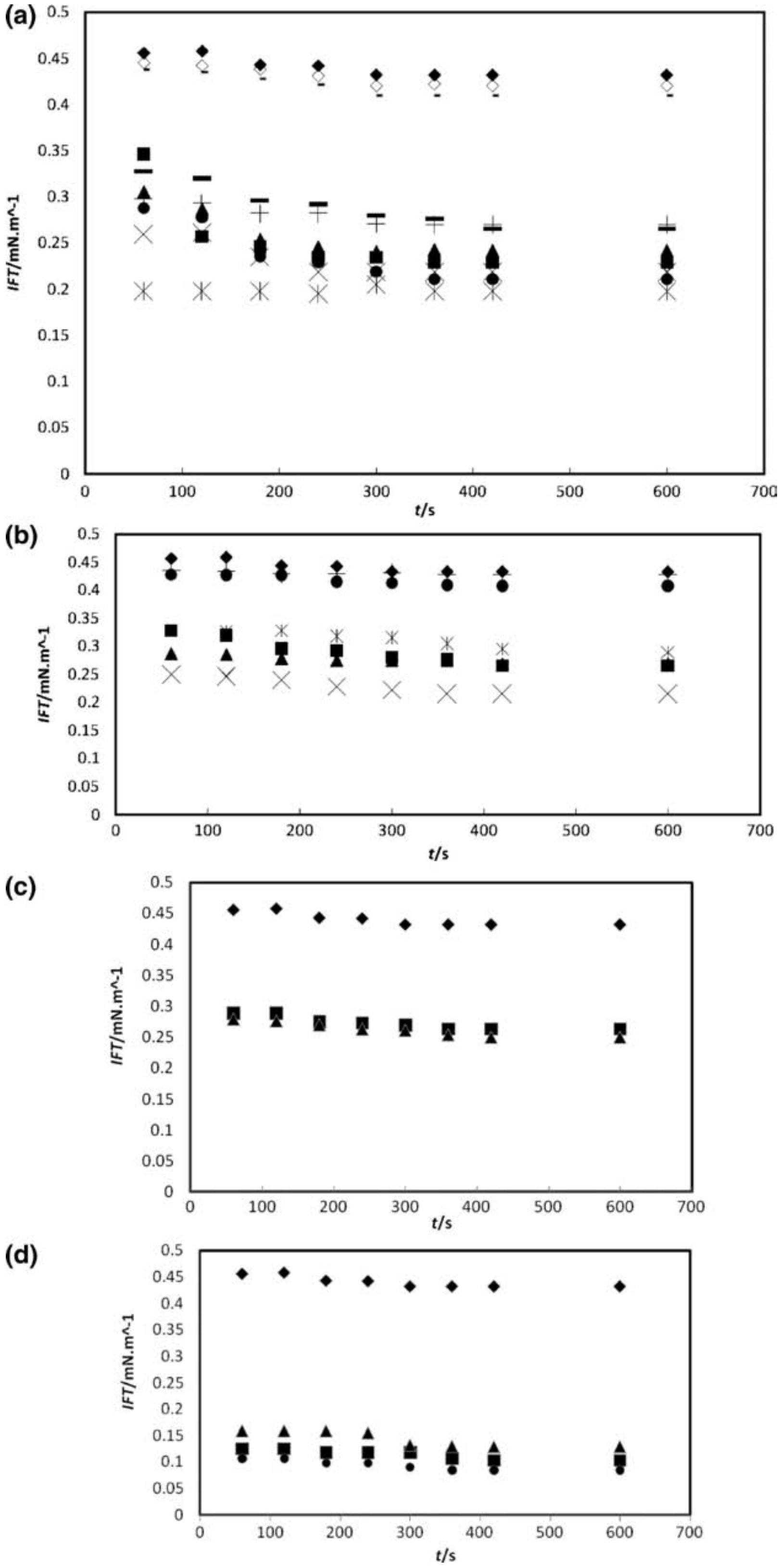

Figure 10. (a) Dynamic interfacial tension (IFT) of various surfactants as demulsifiers: ♦, no demulsifier; ■, MMC; ▲, MCA; ×, BA; ∗, 2-EHA; ●, HA; +, SDS; -, PVP; −, TOMAC; ◇, MA. (b) Dynamic interfacial tension of TOMAC, EC, CO-720, CA-720, KENON10, and KENON20: ♦, no demulsifier; ■, TOMAC; ▲, EC; ×, CO-720; ∗, CA-720; ●, KENON10; +, KENON20. (c) Dynamic interfacial tension of SS and EO/PO block copolymer: ♦, no demulsifier; ■, SS; ▲, EO/PO block copolymer. (d) Dynamic interfacial tension of NPFE and commercial demulsifier formulations, V-4654 and RP-6348: ♦, no demulsifier; ■, NPFE; ▲, V-4654; ●, RP-6348.

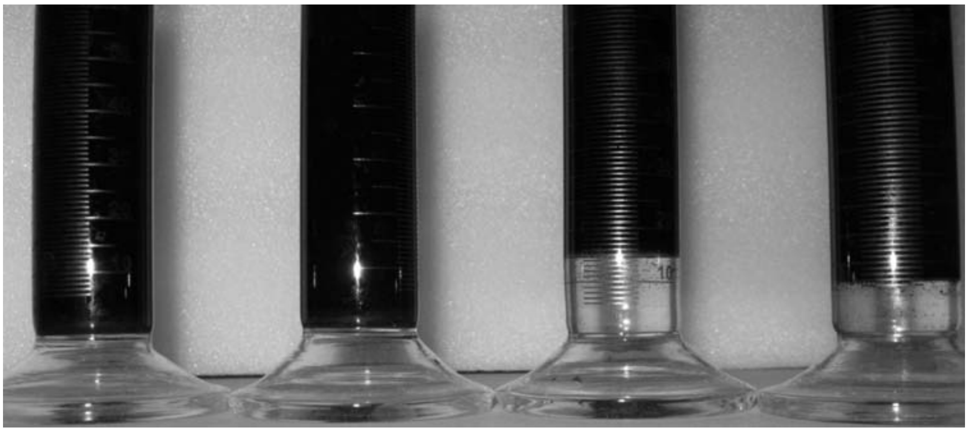

Figure 11. Bottle testing results for choosing the best composite of single chemical demulsifiers for the demulsification of heavy crude oil.

noteworthy that the injection dosage in this run of experiments is $2 \cdot 10^{-4}$ mass fraction, and the operating temperature is 70 °C.

CONCLUSIONS

The effect of different water-soluble surfactant demulsifiers on the stability and properties of medium crude oil emulsions was assessed experimentally via bottle tests. The effect of several water-soluble and oil soluble surfactant demulsifiers on the demulsification of heavy crude oil was also monitored experimentally via bottle tests and dynamic interfacial tension experiments. The results showed that the efficiency of surfactants as demulsifiers was different for the demulsification of medium and heavy crude oils and their efficiency for water separation from the crude oil emulsion was significantly higher for medium crude oil. As was proven before, some surfactant demulsifiers like TOMAC and EO/PO block copolymer and NPFE had better efficiencies at water removal from heavy crude oil emulsions. As was seen in the sets of experiments of dynamic interfacial tension, these materials were those who possessed the lowest interfacial tensions and had the most decrease in interfacial tension by passing time. The final formulation was a formulation consisted of all of these surfactant demulsifiers. These findings can be explained qualitatively in terms of a molecular mechanism that may involve the disruption of the asphaltenic film adsorbed at the water—oil interfaces by the phenolic resins and the formation and expansion of holes between approaching droplets in regions depleted of asphaltenes. The action of the phenolic resins was supplemented by the TOMAC and EO/PO block copolymer, which may act as "bridges" between droplets, thus increasing the probability for collisions leading to successful coalescence events.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +98 711 2303071; fax: +98 711 6287294. E-mail address: rahimpor@shirazu.ac.ir (M.R. Rahimpour).

ACKNOWLEDGMENT

We are thankful to Department of Chemical and Petroleum Engineering, Shiraz University, Iran for providing valuable help to accomplish the research work. Also the authors would like to recognize the support of the South Zagross Gas and Oil Company and also Kimyagaran Emrooz Co.

REFERENCES

(1) Kilpatrick, P. K.; Spiecker, P. M. *Encyclopedic Handbook of Emulsion Technology*; Sjöblom, J., Ed.; Marcel Dekker: New York, 2001; Chapter 30, pp 707—730.

(2) Eley, D. D.; Hey, M. J.; Symonds, J. D. Emulsions of water in asphaltene-containing oils 1. Droplet size distribution and emulsification rates. *Colloids Surf.* **1988**, *32*, 87–101.

(3) Mouraille, O.; Skodvin, T.; Sjöblom, J.; Peytavy, J. L. *J. Dispersion Sci. Technol.* **1998**, *19*, 339–367.

(4) Nordli, K. G.; Sjöblom, J.; Kizling, J.; Stenius, P. Water-in-crude oil emulsions from the Norwegian continental shelf 4. Monolayer properties of the interfacially active crude oil fraction. *Colloids Surf.* **1991**, *57*, 83–98.

(5) Mohammed, R. A.; Bailey, A. I.; Luckham, P. F.; Tayloy, S. E. The effect of demulsifiers on the interfacial rheology and emulsion stability of water-in-crude oil emulsions. *Colloids Surf., A* **1994**, *91*, 129–139.

(6) Kim, Y. H.; Wasan, D. T.; Breen, P. J. A study of dynamic interfacial mechanisms for demulsification of water-in-oil emulsions. *Colloids Surf.* **1995**, *95*, 235–247.

(7) Mason, S. L.; May, K.; Hartland, S. Drop size and concentration profile determination in petroleum emulsion separation. *Colloids Surf., A* **1995**, *96*, 85–92.

(8) Yarranton, H. W.; Hussei, H.; Masliyah, J. H. Water-in-Hydrocarbon Emulsions Stabilized by Asphaltenes at Low Concentrations. *J. Colloid Interface Sci.* **2000**, *228*, 52–63.

(9) Kang, W.; Jing, G.; Zhang, H.; Li, M.; Wu, Z. Influence of demulsifier on interfacial film between oil and water. *Colloids Surf., A* **2006**, *272*, 27–31.

(10) Borges, B.; Rondon, M.; Sereno, O.; Asuaje, J. Breaking of Water-in-Crude-Oil Emulsions. 3. Influence of Salinity and Water—Oil Ratio on Demulsifier Action. *Energy Fuels* **2009**, *23*, 1568–1574.

(11) Ese, M.-H.; Galet, L.; Clausse, D.; Sjöblom, J. Properties of Langmuir surface and interfacial films built up by asphaltenes and resins: influence of chemical demulsifiers. *J. Colloid Interface Sci.* **1999**, *220*, 293.

(12) Zhang, L. Y.; Xu, Z.; Masliyah, J. H. Langmuir and Langmuir-Blodgett films of mixed asphaltene and a demulsifier. *Langmuir* **2003**, *19*, 9730.

(13) Kim, Y. H.; Wasan, D. T.; Breen, P. J. A study of dynamic interfacial mechanisms for demulsification of water-in-oil emulsions. *Colloids Surf., A* **1995**, *95*, 235.

(14) Kim, Y. H.; Nikolov, A. D.; Wasan, D. T.; Díaz-Arauzo, H.; Shetty, C. S. Demulsification of water-in-crude oil emulsions: effects of film tension, elasticity, diffusivity and interfacial activity of demulsifier individual components and their blends. *J. Dispersion Sci. Technol.* **1996**, *17*, 33.

(15) Pena, A. A.; Hirasaki, G. J.; Miller, C. A. Chemically Induced Destabilization of Water-in-Crude Oil Emulsions. *Ind. Eng. Chem. Res.* **2005**, *44*, 1139–1149.

(16) Salager, J. L.; Chattopadhay, A.; Mittal, K. L. *Surfactants in Solution*, Surfactant Science Series; Marcel Dekker: New York, 1996; Vol. 64, issue16, pp 261−295.

(17) Salager, J. L. *Pharmaceutical Emulsions and Suspensions*; Nielloud, F., Marti-Mestres, G., Eds.; Marcel Dekker: New York, 2000; Vol. 2, pp 19−72.

(18) Marquez, N.; Anton, R. E.; Gracia, A.; Lachaise, J.; Salager, J. L. Partitioning of ethoxylated alkylphenol surfactants in microemulsion-oil-water systems. Part II: influence of hydrophobe branching. *Colloids Surf., A* **1998**, *131*, 45–49.

(19) Fan, Y.; Simon, S.; Sjoblom, J. Chemical destabilization of crude oil emulsions: effect of nonionic surfactants as emulsion inhibitors. *Energy Fuels* **2009**, *23*, 4575–4583.

(20) Kim, Y. H.; Wasan, D. T. Effect of demulsifier partitioning on the destabilization of water in oil emulsions. *Ind. Eng. Chem. Res.* **1996**, *35*, 1141–1149.

(21) Buckley, J. S.; Fan, T. Crude Oil/Brine Interfacial Tensions. *Petrophys.* **2007**, *48*, 175–185.