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USING DEMULSIFIERS FOR PHASE BREAKING OF WATER/OIL EMULSION

Amir Mosayebi, Reza Abedini*

*Department of Petroleum Engineering, Mahallat Branch, Islamic Azad University, Mahallat, Iran, *Corresponding author e-mail: reza_abedini20@yahoo.com (R .Abedini)*

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Abstract

Demulsification (emulsion breaking) is necessary in many practical applications as the petroleum industry and waste water treatment in environmental technology. The emulsion stability results from the presence of interfacial barrier preventing coalescence of the dispersed water droplets. The most effective method to overcome the problem is to demulsify the crude by using demulsifiers. The demulsifiers will destabilize the interfacial film between the droplets. Demulsifiers with amine and polymeric groups were used for breaking of water in crude oil emulsion, in this study. The relative rate of water separation were determined via breaker tests. The polymeric group demulsifier had better performance on breaking emulsion than amine group demulsifiers.

Keywords: demulsifier; interfacial film; emulsion; droplet; stabilize.

1. Introduction

Water-in-oil emulsion is formed during the production of crude oil, which is often accompanied with water. The stability of the emulsion is ranging from a few minutes to years depending on the nature of the crude oil and to some extent the nature of water [1].A recent report has suggested that an equivalent volume of water accompanied the daily production of some 60 million barrels of crude oil [2]. Under the production conditions, a proportion of this water can become intimately dispersed throughout the crude oil as small droplets. The natural petroleum emulsion resulting from the secondary production consists of crude oil as dispersion medium and brine as dispersed phase, normally stabilized by natural chemicals such as asphaltenes, resins, solid such as clays and waxes [1]. For asphaltenes in particular, the presence of hetero-atoms in the essentially aromatic structure imparts amphiphilic characteristics [3].

Emulsions are undesirable because the volume of dispersed water occupies space in the processing equipment and pipelines, increased operating and capital costs. Moreover, the characteristics and physical properties of oil change significantly upon emulsification. The density of emulsion can increase from 800 kg/m3 for the original oil to 1030 kg/m^3 for the emulsion. The most significant change is observed in viscosity, which typically increases from a few mPa.s or less to about 1000 mPa.s [4].

Chemical methods are the most common method of emulsion resolution in both oil field and refinery. The application of chemicals designed to neutralize the effects of emulsifying agents have great advantages of being able to break an interfacial film effectively; without the addition of new equipments or modifications of the existing equipment.

2. Materials and Methods

The crude oil applied as model in this study was obtained from the Refinery of Tehran. Specifications and some physical and chemical properties of this crude oil are listed in table 1.

There are wide ranges of demulsifiers that can be used in demulsification of crude oil emulsions. From the literature study, the demulsifiers used in this paper are shown in Table 2. In this study, three demulsifiers, amine groups, polymeric and alcohol were used for water in crude oil emulsions demulsifications. A 500 mL gratuated cylindrical glass was used as sample container.

Table. 1 Specifications and properties of crude oil used as model.

Character	paraffinic
API°	37
Density (g.cm^{-3})	0.8397
Viscosity at 25°C,(cp)	12.6

Table. 2 Types of chemical demulsifiers used as model.

No.	Name	HLB	Concentration (mol.l-1)
1	EO/PO Block Copolymer	9.7	10
2	Hexylamine	4.8	0.5
3	Pentylamine	7.4	0.75
4	Ethyleneglycol (EG)	10	0.35
5	Sodium dodecyl sulfate (SDS)	3.98	0.1

Water in crude oil emulsions were propared at room temperature with a mixer at speed 1200 rpm. First, distilled water was used as water phase (dispersed phase) and crude oil as oil phase (continuous phase). The emulsifiers used in this study for emulsion formulation were ethoxylated nonyl phenols. For different demulsifiers, water in crude oil emulsions were prepared and tested.

The water separation in percent was calculated as separation efficiency from volume of water observed in the breaker as follows:

$$\%\ water\ separated\ \ (mL\ /\ mL) = \frac{Volume\ of\ separated\ water,\ mL}{original\ volume\ of\ water\ \text{ in }\ the\ emulsion,\ mL} \times 100$$

Tables 3 and 4 shows the effect of different demulsifiers on crude oil emulsion stability (% water and oil separation), respectively.

Table. 3 The effect of different demulsifiers on crude oil emulsion stability (% water separation mL/mL).

Time (min)	EO/PO Block Copolymer	Hexyl amine	Pentyl amine	Ethylene glycol (EG)	Sodium dodecyl sulfate
0	0	0	0	0	0
100	5	3	1	0	0
200	7	7	2	0	0
334	16	9	4	2	1
468	20	10	7	5	4
692	23	13	11	6	6
820	29	14	13	9	10
1000	31	18	15	14	12
1185	38	21	19	17	13
1420	44	23	20	18	16
1600	45	26	22	20	18
1850	49	32	24	22	19
2200	55	34	26	22	20
2800	55	34	29	22	20
3200	55	34	29	22	20

Table. 4 The effect of different demulsifiers on crude oil emulsion stability (% oil separation mL/mL).

Time	EO/PO Block Copolymer	Hexyl amine	Pentyl amine	Ethylene glycol (EG)	Sodium dodecyl sulfate
0	0	0	0	0	0
100	6	3	0	1	0
200	9	6	2	4	0
334	17	10	3	8	3
468	23	14	6	12	6
692	27	17	9	15	8
820	32	19	11	19	10
1000	38	22	16	21	13
1185	42	24	18	24	14
1420	47	27	21	26	17
1600	50	29	24	28	20
1850	53	31	27	28	22
2200	57	35	29	28	23
2800	57	35	29	28	23
3200	57	35	29	28	23

3. Results and Discussion

Figure 1 and 2 show separation of water and oil from water in oil emulsions as a function of time, respectively. The process of chemical demulsification of a water in crude oil emulsion involves the acceleration of the coalescence as well as the film rupture process. Dispersed water droplets approach each other and flatten to form a thin film of continuous oil phase between them, the outward drainage flow of the film can create gradients in interfacial tension which then oppose and slow down such drainage [5]. The tendency for the drops to coalesce will be the van der Waals forces when the lamellae are thin enough, and the restoring forces will be the Gibbs-

Marangoni effect (figure 3). This effect will operate due to the distortion and increase in surface area of the drops as they get close together. So, it can be concluded that the stability of emulsions is largely affected by the nature of the interfacial film and surfactant adsorption mechanisms [6]. As shown in figure 1, after 200 min, the amount of water separated from water in crude oil emulsion for EO/PO Block Copolymer, hexyle amine, pentyl amine, ethylene glycol and SDS were 7, 7, 2, 0 and 0 %, respectively. After 1000 min, there was no further water separation observed in the entire sample tested. After a long duration (2200 min), EO/PO Block Copolymer had separated water highest percentage (55 %), followed by hexyle amine (34 %), pentyl amine (29 %), ethylene glycol (22 %) and SDS (20 %), respectively.

As shown in figure 2, it was found that the percentage of oil separation from water in crude oil emulsions were more than water separation in the entire sample tested. After a long duration (2200 min), EO/PO Block Copolymer had separated water highest percentage (57 %), followed by hexyle amine (35 %), pentyl amine (29 %), ethylene glycol (28 %) and SDS (23 %), respectively. SDS had Lowest percentage of water and oil separation in the entire sample tested.

The effectiveness of emulsion breaking between the amine group demulsifiers and polymeric can be compared in terms of their ability in separating the water and oil from emulsions. Experimental results obtained in this study, it was founded that the polymeric demulsifiers were more effective in emulsion breaking than amine group demulsifiers.

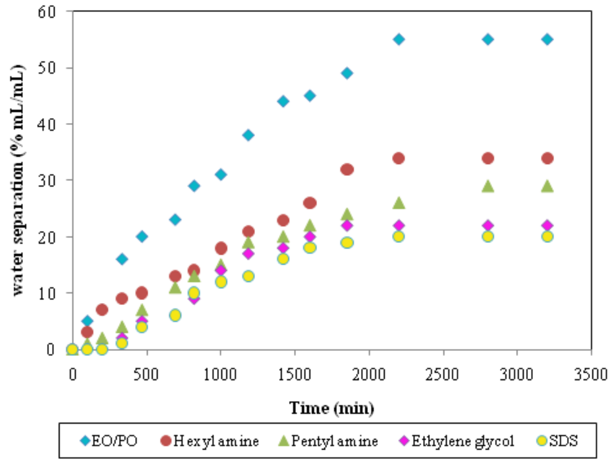

Fig. 1. The effect of different demulsifiers on crude oil emulsion stability (percentage of water separation)

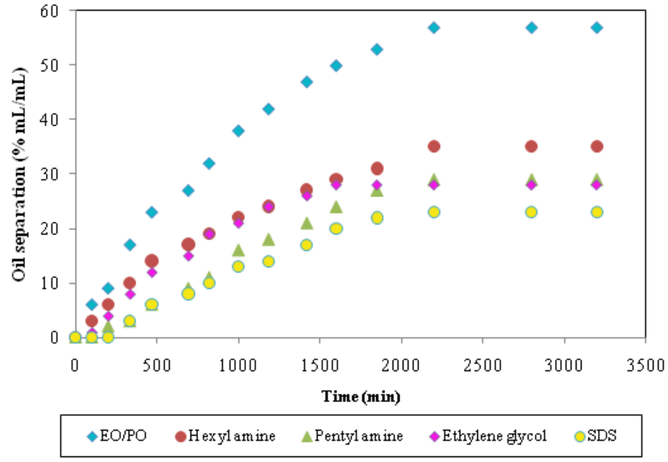

Fig. 2. The effect of different demulsifiers on crude oil emulsion stability (percentage of oil separation)

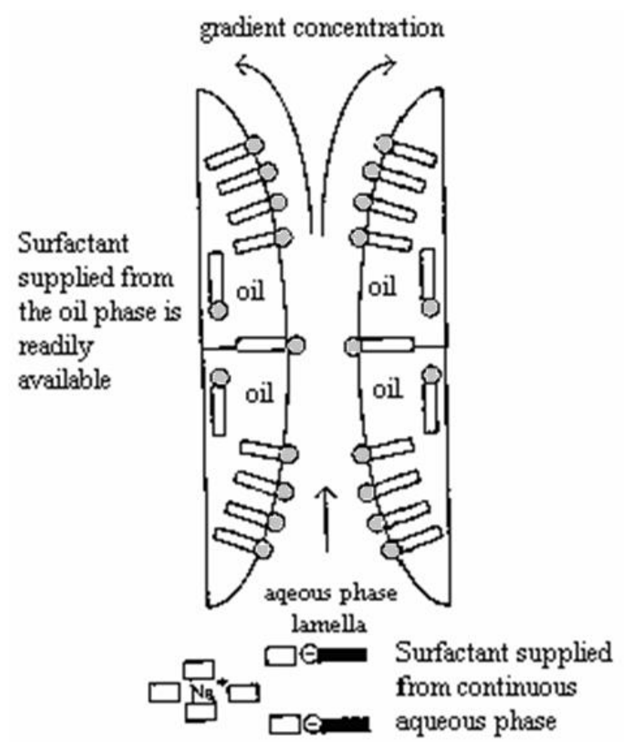

Fig. 3. The Gibbs-Marangoni effect [7].

4. Conclusions

Crude oil in the reservoir is found together with formation water. The stable emulsion resulted from the stress caused from the flow of crude oil and formation water. Emulsions create a lot of problems such as corrosion. For these reasons, crude oils must be treated by using demulsifiers.

Demulsifiers accelerate the emulsion breaking process. The demulsifier adsorbs at the interfacial film, weaker the interfacial barrier and separate the water droplets. The amine and polymeric group demulsifiers wrer used for breaking of water in crude oil emulsion. Polymeric group demulsifiers were more effective in emulsion breaking than amine group demulsifiers.

Polymeric group demulsifier obtained 55 % water and 57 % oil, respectively.

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