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THE EFFECT OF NON-IONIC SURFACTANTS ON THE INTERFACIAL TENSION BETWEEN CRUDE OIL AND WATER

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Abstract

In this study, the effect of non-ionic surfactants on the interfacial tension between crude oil and water were investigated. The interfacial tension was measured by rising drop technique. The interfacial tensions decreased significantly in concentration range of (0-1.25 $g.l^{-1}$). By increasing of temperature, the time needed for an interfacial tension to reach equilibrium reduced. The effect of mixed surfactants on the decreasing of the interfacial tension was more to contrast with individual surfactant, because of the synergism.

Keywords: Surfactant; Enhanced oil recovery; Interfacial tension; Critical micelle concentration.

1. Introduction

Surfactants are special classes of molecules that are both hydrophobic and hydrophilic; hence the most stable configuration for these molecules is at the crude oil and water interface. These molecules are generally injected in order to reduce the interfacial tension between crude oil and water. The interfacial tension plays a fundamental role in conventional and enhanced oil recovery (EOR) methods. The use of surfactants in enhancing oil recovery has generally based on the reduction of the interfacial tension between the crude oil and the flooding phase. This procedure can be performed by reducing the capillary forces to improve the microscopic displacement efficiency [1].

Various parameters such as purity of surfactant, class of surfactant, mineral salt, pH and temperature are effective on the performance of surfactant. Purity of the surfactant has a huge impact on the surface tension and interfacial tension. According to previous investigations, if there is a small amount of impurity in the surfactants, interfacial tension has the different treatment against the surfactant concentration and it can be seen minimum values of interfacial tension vicinity to critical micelle concentration [2].

Among the classes of surfactants, non-ionic and anionic surfactants have considerably more effect on the interfacial tension compared to other surfactants. The temperature increases the diffusion and adsorption velocities of surfactants at the interface. Therefore, temperature has remarkable effect on the interfacial rheological properties.

Effect of ethoxylated nonyl phenols as non-ionic surfactants with ethoxy group numbers 4 and 9 (nonyl phenol 4 and nonyl phenol 9) on the interfacial tension between crude oil and water were investigated, in this study. These surfactants can be classified as good interfacial tension reducer and wetting agent. These classes of surfactants are very suitable for reducing of interfacial tension when used in conjunction or with other surfactants in specially designed formulations. Bedő et *al.* [3] extensively studied micellization, structure of micelles and the thermodynamic parameters of micellization of the ethoxylated nonyl phenols.

2. Experimental

The crude oil applied as model in this study was obtained from the Refinery of Tehran. Before measurement of interfacial tension crude oil was dehydrated by centrifugation. Specifications and some physical and chemical properties of this crude oil are listed in table 1.

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

Surfactants used in this study were obtained from Kimyagaran Emrooz, chemical industry company, Iran. Specifications and some physical and chemical properties of these surfactants are listed in table 2.

Table. 2. Specifications and properties of two surfactants.

Trade name	Nonyl phenol 4	Nonyl phenol 9
Physical form	Clear, viscous liquid	Clear, viscous liquid
Type of surfactant	Non-ionic	Non-ionic
Viscosity at 23°C (cp)	220	320
Density at 23°C ($g.ml^{-1}$)	1.02	1.06
pH (5% solution in water)	6	6.5
Polyethylene glycol, percent	2	2
Hydroxyl Value, $mgKOH.g^{-1}$	143	91
Cloud point (10% in water), °C	57	51
Water,percent	0.5	0.5

The experiments were performed using interfacial tension meter of DBR. The interfacial tension measurements were carried out with rising drop method. This method allows the formation of a drop of one fluid at the tip of a hollow needle which is submerged in the second phase. Drop formation is performed under controlled temperature and pressure, with the maximum drop size recorded photographically. Using the drop dimensions on the photo-graphic image, and known needle dimensions, software WIN.DROP (for measuring of each sample, error of software is ±0.0001 $mN.m^{-1}$) can determine the interfacial tension for a selected fluid [4].

3. Results and Discussion

Fig. 1 shows the plot of interfacial tension against the surfactant concentration at the temperature of 25°C. There was no minimum value at the vicinity to critical micelle concentration (for nonyl phenol 4 was 0.664 g.l-1 and for nonyl phenol 9 was 0.747 g.l-1), so were pure both surfactants used in this paper.

In concentration range of (0-1.25 g.l-1), the interfacial tensions of nonyl phenol 4 and nonyl phenol 9 decreased of 27.86 mN.m-1 to 1.85 mN.m-1 and 2.63 mN.m-1, respectively at 25°C. It shows which both surfactants had remarkable effect on the interfacial tension between crude oil and water.

For the interfacial tension to reach its equilibrium value surfactants first must diffuse into the interface, then adsorb in the interfacial film, this procedure can well be characterized by dynamic interfacial tension (DIT). Fig. 2 is the plot of interfacial tension against time. The time which was needed for an interfacial tension to reach equilibrium reduced, when temperature increased.

The increasing of temperature led to increase mutual solubility of the solvents, lipophilicity of surfactants and diffusion velocity of surfactant molecules onto the interface, adsorption velocity of surfactant molecules at the interface and reduction of critical micelle concentration. Furthermore, it caused time which was needed to reach equilibrium interfacial tension reduced, so it affected the dynamic interfacial tension.

Both surfactants were non-ionic, so the mixture of two surfactants led to synergism. There was a spatial repulsion among molecules of non-ionic surfactants. When these molecules approached, the spatial repulsion would increase, so it caused critical micelle concentration to increase [5]. Interfacial tension between crude oil and surfactant solution was measured at different concentrations of mixture of two surfactants (mass ratio of nonyl phenol 9 and nonyl phenol 4 was 1) at 25. The results are shown in table 3.

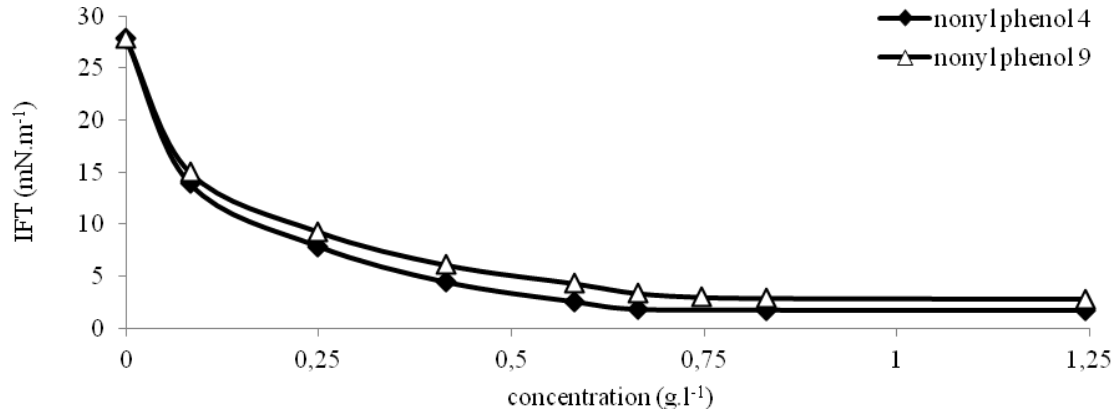

Fig. 1. The interfacial tension as a function of surfactant concentration, at 25°C.

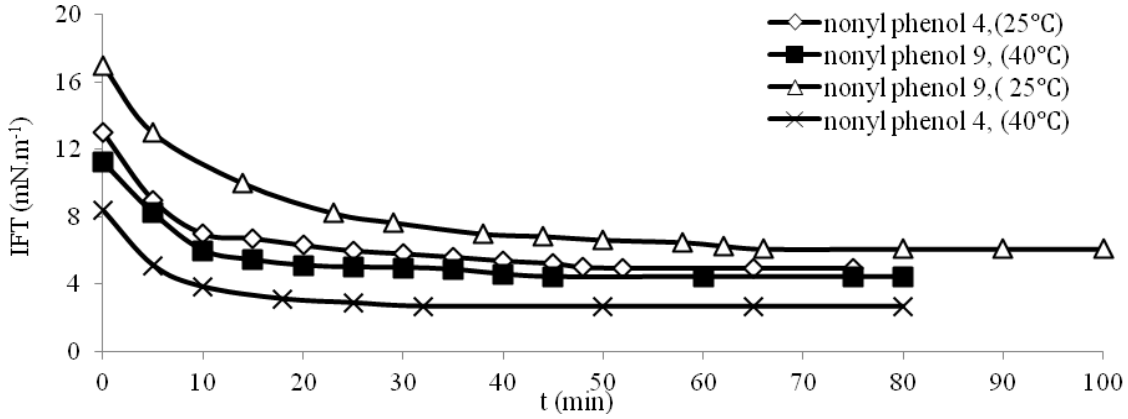

Fig. 2. The interfacial tension as a function of time, the surfactant concentrations is 0.415 $g.l^{-1}$.

Results were shown when two surfactants were mixed, critical micelle concentration would increase. The critical micelle concentration for mixed surfactants was 1.079 $g.l^{-1}$ (critical micelle concentration for nonyl phenol 4 was 0.664 $g.l^{-1}$ and for nonyl phenol 9 was 0.747 $g.l^{-1}$).

Table. 3. The effect of concentration of mixture of two surfactants on interfacial tension at 25°C

Concentration of mixture of two surfactants ($g.l^{-1}$)	0	.1	.4	0.625	0.83	.95	1.079	1.25
mass ratio of nonyl phenol 9 and nonyl phenol 4	1	1	1	1	1	1	1	1
IFT ($mN.m^{-1}$)	27.86	18.23	6.67	2.3	0.749	.134	0.049	.044

The aggregation of surfactant molecules resulted from mixed surfactants which named mixed micellar aggregates. As formation of mixed micellar aggregates, mixed surfactants had more influence on reduction of interfacial tension to contrast with individual surfactant. Therefore, when two surfactants were mixed, interfacial tension significantly decreased.

4. Conclusions

In this paper, the effect of ethoxylated nonyl phenols on the interfacial tension between crude oil and water was investigated. In concentration range of (0-1.25 $g.l^{-1}$), interfacial tensions of nonyl phenol 4 and nonyl phenol 9 decreased of 27.86 $mN.m^{-1}$ to 1.85 $mN.m^{-1}$ and 2.63 $mN.m^{-1}$, at 25 respectively. For mixture of two surfactants, because of formation of mixed

micellar aggregates, mixed surfactants had more influence on reduction of interfacial tension than individual surfactant.

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