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MALAYSIAN CRUDE OIL EMULSIONS: STABILITY STUDY

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Abstract

The stability of water-in-oil emulsion of some Malaysian crude oils was studied with particular emphasis on the effect of interfacial active components existed in the crude oil, i.e. asphaltene, resin and wax. The emulsion stability was studied by measuring the volume of water or oil phase separated in variation with time, water hold up and the heights of the sedimenting/coalescing interfaces during the separation at various temperatures. The study investigated the influence of asphaltene, resin and wax on emulsion stability if it's present in the crude oil alone, together or combination one of the others. The results show that the interfacial active components that stabilize emulsion is asphaltene. The resin and wax do not form stable emulsion either alone or together. There is a correlation between emulsion stability and physicochemical properties of crude oil which showed that higher asphaltene content in the crude oil would form more stable emulsion. Increased temperature was found to cause instability of the emulsion.

Keywords: emulsion stability, crude oil, asphaltene, resin, and wax.

Introduction

Emulsion is generally considered being the dispersion of one liquid in another with which it is immiscible. The emulsion consists of three phases: the internal, external and interface. The internal or dispersed phase presents in the form of finely divided droplets while the external or continuous phase forms the matrix in which the droplets are suspended. In order to the system to be stable for long time, a third constituent must present, has known as interfacial active agent or surfactant. In general, emulsion is divided into two liquid phases. If the oil is dispersed in the water, the emulsion is of the oil-in-water type (o/w), with the oil being the dispersed phase and water being the continuous phase. If the phases are reversed, so that the water is dispersed in the oil, the emulsion is of the water-in-oil type (w/o). Water–in-oil emulsions are generally referred to as *invert* emulsions (Becher, 1955).

In the petroleum industry, water-in-oil emulsions are common. Water-in-oil emulsion is less sensitive to pH, sensitive to heat, amenable to electrical treatment, has a lower electrical conductivity, is ready coloured by oil soluble dyes, and can be diluted by adding more pure oil. The converse is true for the oil in water system. Crude oil emulsion stability has been the subject of intense research during the last decades and there is a need for more basic research in order to understand the mechanisms governing the stability of oil-continuous emulsion. Emulsion is stable, if the repulsive forces between the dispersed droplets are sufficiently strong and the dispersed phase has sufficiently limited mobility in the direction of the external force field (Schubert and Armbruster, 1992). The repulsive forces prevent aggregation and coalescence of the droplets while the restricted mobility prevents the droplets from settling. As reported in the literature that asphaltene and resin fraction together with waxes could stabilize the water-in-crude oil emulsion (Johansen, et al, 1989; Schildberg, Sjoblom and Christy, 1995). Waxes can act either on a molecular level as lipids or as particles in the interfacial film, or alternatively as viscosifier in the continuous oil phase; hence, changes interfacial activity. There is a clear correlation between a high content of wax particles and a high viscosity. Furthermore, the role of waxes is important to investigate beside asphaltene and resin in order to understand how far the influence of the resin/asphaltene/wax ratio on the stability of water-in-crude oil emulsion. Although, results of the study have been reported in the literature, the fundamental aspect of the crude oil emulsion stability has not been clear, especially on the effect of physical and chemical properties of the crude oil emulsion. When the stability of an emulsified system is discussed, there is approximation to be considered. The approach deals with the overall behaviour of the crude oil emulsions system, which include physical and chemical properties of them. Is there any correlation between the properties on emulsion stability? How

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far the roles of natural surfactants such as asphaltenes, resins and waxes in stabilising the emulsion.

In order to elucidate those questions, we carried out experimental study which was focused on: (1) the study on stability of water-in-oil emulsion based on Malaysian crude oils in relation to their physical and chemical properties; and (2) the influence of asphaltene, resin and wax on emulsion stability if they are present in the crude oil alone, together or combination one of the other. This paper will present some our preliminary results on the subject understudy.

Experimental

Chemicals

Crude oil samples

Six different crude oil samples were used in this experiment: COE1, COE2, COE3, COE4, COE5 and COE6. Results of chemical analysis of these crude oil samples are given in Table 1.

Synthetic oilfield brine

The synthetic oilfield brine used in this experiment was prepared by dissolving NaCl in double distilled water to obtain the solution with salinity of 9.4 ‰ which is equivalent to the salinity of the oilfield brine sample of COE1.

Chemicals

All chemicals were used without further purification. Pentane (GC > 98%; J.T. Beker), dichloromethane (100%; Mallinckrodt), Methanol (99.9%; Mallinckrodt), were used as solvents. NaCl (99.8%; R&M Chemicals), Decane (99%; BDH) were used in preparing model emulsion systems, while silica (55-105 micron; Millipore Corporation) was used as an adsorbent in separation of interfacial active fraction.

Methods

Separation of interfacial active fraction

The crude oil was agitated with pentane (ratio 1:5) at room temperature for 10 minutes. The mixture was then left rest to equilibrate for 1 hour and then centrifuged at 3000 rpm at room temperature for 10 minutes until the asphaltene fraction precipitated. Silica was added to the supernatant until the solution was nearly colorless. The silica containing adsorbed component of resin was recovered. The adsorbed fraction was then dissolved in a mixture of 7% methanol in dichloromethane. The resin fraction finally obtained by evaporating of the methanol-dichloromethane mixture(Ese, et. Al, 1997).

Emulsion preparation and stability testing

The real emulsion sample was prepared by mixing the crude oil with oilfield brine (ratio 1:1 v/v). The emulsification process was carried out using an Ultra Turrax T50 homogenizer, for 2 minutes at 8000 rpm. Stability of the emulsion was determined by measuring the water concentration or hold up profile with time at room temperature. The testing was done by using the glass column equipped with sampling pots. The water concentration was measured by using Karl Fischer method. In order to understand the effect of asphaltene, resin or wax on emulsion stability, the above procedure was repeated but using synthetic emulsion system. The asphaltene, resin, wax or their combinations were added to the model system either decane-synthetic oilfield brine (decane system) or saturated hydrocarbon-synthetic oilfield brine HC system). The saturated hydrocarbon is the crude oil free interfacial active fraction obtained from separation of interfacial active component experiments. Stability of the emulsion systems was determined by measuring the water and oil separated from the systems with time.

Table 1: Chemical properties of crude oil samples.

Types of crude oil sample	Chemical analysis					
	Asphaltene (% w/w)	Resin (% w/w)	Saturated Hydrocarbon (% w/w)	Wax (% w/w)	**Volatile matter** (% w/w)	Water content (% w/w)
COE1	1.35	35.32	33.24	11.81	15.35	2.93
COE2	0.55	36.43	43.38	13.41	1.69	4.54
COE3	0.13	32.01	44.96	15.37	4.62	2.91
COE4	0.08	20.94	55.51	9.13	13.95	0.39
COE5	0.06	29.81	51.78	8.68	9.26	0.41
COE6	0.37	21.50	24.97	13.42	22.03	17.71

Results And Discussion

Stability of the various crude oil emulsions

Figure 1 shows a profile of water hold-up or water concentration at different height position for various crude oil emulsions. The emulsions were observed for 30 days. Actually, the water separation phenomena in the column test take place as follows. Initially, when the emulsion is still homogeneous the hold-up of all crude oil emulsions is nearly a vertical line (50%). As sedimentation and coalescence take place, separation of water and oil from the emulsion could be observed. The water hold up in the upper part of the column test approach to zero, clear oil observed because the water droplets have precipitated out. In the lower part separation takes place as water hold up gradually increases toward 100 %, indicating a dense-packed zone of water droplets. Emulsion is stable if the hold-up profile does not follow the breakdown process as above, in the other word after a long time the hold-up profile is nearly a vertical line. On the other hand the emulsion is not stable if after a period of time the hold-up profile in the upper part and the lower part is zero and 100 %, respectively (Panoussopoulos, 1998; Mason, et.al, 1995).

The results of this experiment show that the COE1 and COE3 formed most stable emulsion followed by COE2, COE6, COE5 and COE4. These results are in accordance with chemical analysis of crude oil as shown in Table 1. The COE1 forms the most stable emulsion because it has higher asphaltene content than others, resin-asphaltene ratio is the lowest, high wax content and high suspended matter. On the other hand, the COE4 and COE5 are the most instable. The higher asphaltene content will result higher crude oil emulsion stability. The most interesting observation is the existence of correlation between resin-asphaltene ratio and stability. The resin-asphaltene ratio of COE1, COE2, COE3, COE4, COE5 and COE6 is 26, 66, 246, 261, 496 and 58, respectively. Increasing in resin-asphaltene ratio decreases in emulsion stability. This result is in accordance with previous experiment done by Schorling et al, 1999. They have found that the resin-asphaltene ratio clearly influences on emulsion stability. As the resin-asphaltene ratio increases, the emulsion stability decreases.

The present of suspended matter in the COE1, COE3, COE6 and COE2 also enhances crude oil emulsion stability. Stability increases if any fine solid particles lying at the interface between oil and water phases preventing droplet coalescence and, when repulsive forces between the particle are present, it will prevent aggregation of droplets (Schubert and Armbruster, 1992; Tambe and Sharma, 1993). Wax can change interfacial activity by acting either as lipids or as particles in the interfacial film. Wax content of the COE3 is the highest, as a result, it forms most stable emulsion.

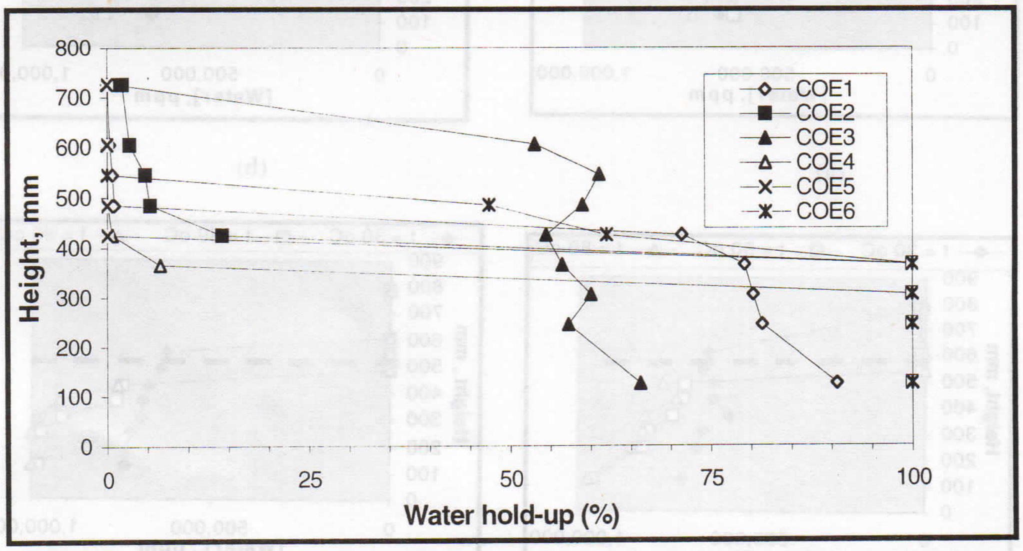


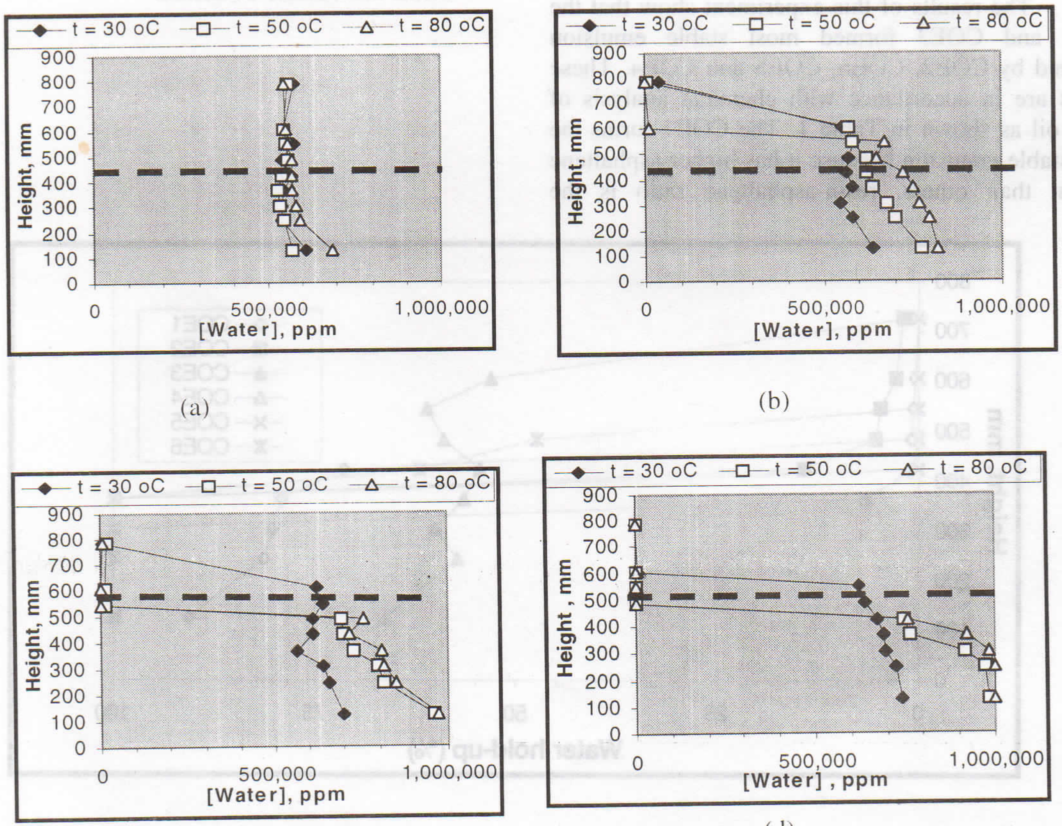
Figure 1: Hold-up and water concentration profiles of separation process from various crude oil emulsions at 30 °C.

Influence of temperature on emulsion stability

The effect of temperature on emulsion stability study was carried out by preparing emulsion using COE1 crude oil. Stability study was carried out by using double wall glass column equipped with temperature control system. Figure 2 shows the influence of temperature on emulsion stability. The results show that the effect of temperature is significant, especially at higher temperatures. Figure 2a shows that after 1 day the emulsion is still relatively stable, the water concentration was uniform at any position, its mean that the system was homogeneous. After 7 days the separation process takes place between oil and water phases. Separation rate increases with increasing temperature as shown in Figs. 2c and 2d. For the 80 °C , the completed separation of emulsion was observed after 30 days.

Figure 3 shows the separation profiles at various temperature that can be distinguished between the sedimenting and coalescing interfaces. For 80 °C, either the sedimenting or coalescing interface reaches almost final interface (middle line) after 30 days, which means that the complete separation of water and oil phase is reached. For 30 °C, there is no significant water separation observed and the coalescing interfaces shows as horizontal lines.

The temperature can cause changes in the interfacial tension between oil and water phases, the viscosity of the interfacial film, the relative solubility of emulsifying agent in the two phases and the thermal agitation of the dispersed droplets (Zaki, et.al, 1996). Asphaltene is considered to be the main factor controlling the stability by forming a stable viscoelastic film, which prevents water droplets to approach closer to each other for coalescing to occur (Tambe, et.al, 1995). Increasing the temperature causes a decrease in interfacial shear viscosity, consequently increasing the rate of film drainage. The increase in temperature also increases the number of collisions occurring between two dispersed water droplets prior to their coalescence. Finally, increasing the temperature will cause density difference between dispersed and continuous phases to be large enough, resulting in enhancing emulsion breakdown.



(a) (b)

(c) (d)

Figure 2. Influence of temperature on emulsion stability at various times: (a) 1 day; (b) 7 days; (c) 15 days; (d) 30 days.

Influence of interfacially active fraction on emulsion stability

Asphaltene and resin are structuraly similar but difference in their molecular weight. Both contain polyaromatic rings bearing alkyl and alicyclic systems with heteroatom. Number of rings in resins is smaller than asphaltenes and therefore the molecular weight of resins is smaller. Asphaltenes are more aromatic than resins and have low H/C ratio compared to resins. The presence of OH and carbonyl group in asphaltenes can form a mechanical barrier through the formation of hydrogen bonding around the water droplet to prevent coalescence. The presence of carbonyl group alone in resins molecule is not sufficient to form a strong hydrogen bonding at the interface in order to prevent the coalescence (Mingyuan, 1992).

In order to study the influence of interfacial active fraction namely asphaltene, resin and wax on stability of oil emulsion, it requires to prepare two models emulsion system: (1) hydrocarbon free interfacial active fraction – synthetic oilfield brine (HC System); and (2) decane - synthetic oilfield brine (decane System), both stabilized with asphaltene, resin, wax or combination of them. The reason for utilizing these two models emulsion system is to compare them, so one can understand how far the influence of various hydrocarbon constituents in real sample on stability. As one know that the crude oil contains a very complicated mixture of hydrocarbon, which is very difficult to describe with precision on the nature of the hydrocarbon present in crude oil samples.

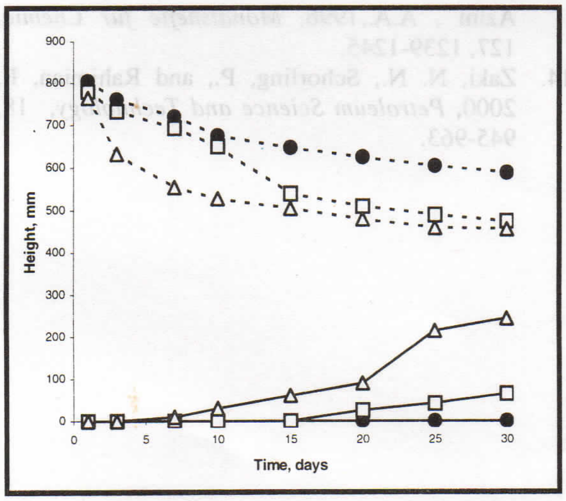


Figure 3. Separation behavior of COE1 emulsion at various temperatures.

Figures 4 and 5 show the effect of natural surface active agent on emulsion stability either for HC or decane system. The surface-active components such as asphaltene, resin or wax were added to the system with composition similar to those obtained from the chemical characterisation of the COE1 sample. For HC system, Fig. 4 demonstrates that the emulsion systems i.e. HC, HC+W, HC+R, and HC+R+W which no asphaltene content show most instable emulsion as indicated by complete water separation within 30 minutes. But for the systems which consist of asphaltene i.e. HC+A, HC+A+R, HC+A+W and HC+A+R+W are most stable where there are no significant water separation observed up to 10 days. The results showed that the asphaltene alone or together with wax/resin could stabilize the emulsion, whereas resin or wax without asphaltene could not. This result confirms to experiment results reported by Zaki et al. (2000). Their experiment had found that resins alone do not capable of stabilizing the emulsion, however, in the presence of asphaltene they could form very stable emulsion .

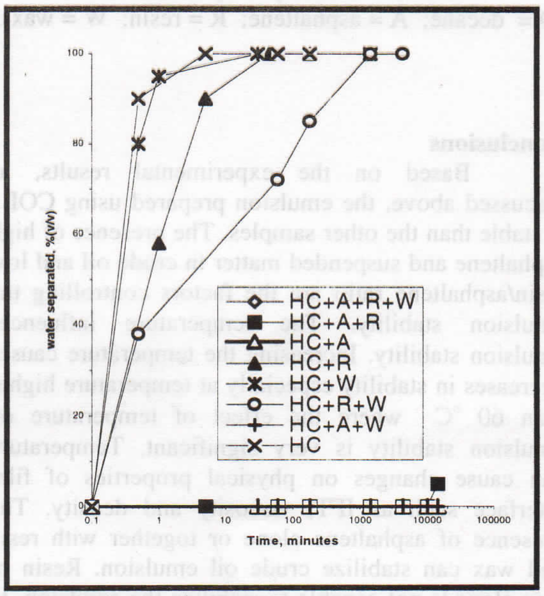


Figure 4. Effect of natural surface-active agents on emulsion stability of preparing using hydrocarbon free active fraction (HC system). (HC = saturated hydrocarbon isolated with free interfacial active fraction; A = asphaltene; R = resin; W = wax).

In general, both systems, HC and decane emulsion systems show a significant difference in term of water separation characteristics. The decane emulsion system was stable than HC system. The HC emulsion system achieved complete separation after 5 minutes while the decane system was after 0.5 minutes. It is therefore realized that a complicated mixture of hydrocarbons existed in the crude oil plays an important role in enhancing emulsion stability.

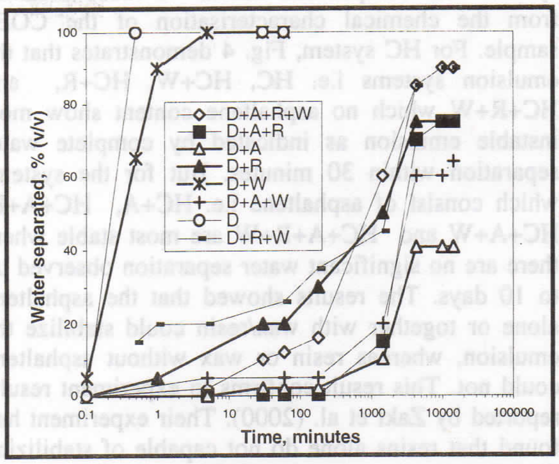


Figure 5. Effect of natural surface-active agents on emulsion stability of synthetic oil.

(D = decane; A = asphaltene; R = resin; W = wax).

Conclusions

Based on the experimental results, as discussed above, the emulsion prepared using COE1 is stable than the other samples. The presence of high asphaltene and suspended matter in crude oil and low resin/asphaltene ratio are the factors controlling the emulsion stability. The temperature influences emulsion stability. Increasing the temperature causes decreases in stability especially at temperature higher than 60 °C where the effect of temperature on emulsion stability is very significant. Temperature can cause changes on physical properties of film interface such as IFT, viscosity and density. The presence of asphaltene alone or together with resin and wax can stabilize crude oil emulsion. Resin or wax alone is not capable to stabilize the emulsion. In general, the real emulsion systems are more stable than the synthetic emulsion system and this indicates that the presence of various hydrocarbon constituents in the real sample influences on emulsion stability.

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