



# Journal of Applied Sciences

ISSN 1812-5654

**science**  
alert

**ANSI***net*  
an open access publisher  
<http://ansinet.com>

## Stabilization Mechanisms of Water-in-Crude Oil Emulsions

<sup>1</sup>Abdurahman H. Nour, <sup>1</sup>A. Suliman and <sup>2</sup>Mahmmoud M. Hadow

<sup>1</sup>Faculty of Chemical and Natural Resources Engineering,

University Malaysia Pahang-UMP, P.O. Box 12, Locked 25000, Kuantan, Malaysia

<sup>2</sup>Faculty of Electrical Engineering, University Technology Malaysia, UTM, Malaysia

---

**Abstract:** During the lifting and production of crude oil, water/oil emulsions are created. They are stabilized by asphaltenes and resins which are colloiddally dispersed in the crude oil. Asphaltenes consist mainly of polar heterocompounds. It is known that they decrease the interfacial tension between oil and water and form stable interfacial films. Both effects favour the formation and stabilization of emulsions. Resins are complex high-molecular-weight compounds that are not soluble in ethylacetate, but are soluble in n-heptane. Their interfacial activity is less than that of asphaltenes. The role of resins in stabilizing emulsions has also been debated in literature. This study reports the results of experimental investigation of various factors affecting the stability of emulsions which are considered to be undesirable for a number of reasons, including both up-stream and down-stream operation in the petroleum industry. It was found that, the (R/A) ratio affects the emulsion and dispersion stabilities. High resin/asphaltene ratios decrease the emulsion stability.

**Key words:** Viscosity, resin, asphaltene, stability, w/o emulsion, R/A ratio

---

### INTRODUCTION

Water is normally present in crude oil reservoirs or is injected as steam to stimulate oil production. Water and oil can mix while rising through the well and when passing through valves and pumps to form in most cases relatively stable dispersions of water droplets in crude oil (w/o), which are usually referred to as oilfield emulsions. The formation of emulsion creates problems during the production, transport of multiphase oil-water-gas mixture to the land based process plants from the production sites. Formation of these emulsions during oil production is a costly problem, both in terms of chemicals used and due to production losses. Environmental problems arise because of the difficulty in cleaning up of the environment after oil-spillage by techniques such as burning, use of sorbants, use of dispersants and pumping (Mingyuan *et al.*, 1992). To reduce the water content of the produced crude oil, the water/crude oil emulsions have to be broken (demulsified). Thus, it is important to understand the mechanisms responsible for stabilization of these emulsions (Berger *et al.*, 1987; Mohammed *et al.*, 1993a, b, c; Sjoblom *et al.*, 1990a, 1992, 1995). The effect of asphaltene solvency on the stability of water-in crude oil emulsions reported (Kilpatrick and McLean, 1997). The role of asphaltenes in the stability of water-in-bitumen emulsions has recently been studied (Yan *et al.*, 1999). Depending on the crude oil aliphatic/aromatic ratio which governs the solubility of asphaltene-resins and their

interfacial activity, one can expect three major stabilization mechanisms for a crude oil film between water deposits (Wasan and Nikolov, 1993; Krawczyk *et al.*, 1991). (1) steric stabilization due to an adsorbed layer of asphaltene at a low concentration of asphaltene-resin submicron particles; (2) depletion destabilization due to an excluded volume effect, leading to attraction between water droplets and (3) structural stabilization due to long-range colloidal structure formation inside the film in the presence of a sufficient effective volume fraction of colloidal particles. Stable water-in-oil emulsions are characterized by a high water content (50 to 90%), high viscosity, small water droplets and higher density than the original oil (Brandvik and Daling, 1991; Fingas *et al.*, 1994). Stable emulsions have been defined by Fingas *et al.* (1994) as emulsions in which the water persists for 5 days or longer. The high viscosity of stable emulsions results in a semisolid or gel formed from the liquid crude oil. The size of water droplets in water-in-oil emulsions has been investigated by light and electron microscopy (Mikula, 1992). Crude oil from the Norwegian continental shelf formed emulsions containing water droplets with dimensions in the 10 to 30  $\mu\text{m}$  range (Sjoblom *et al.*, 1990b).

The aim of this study is conducted to investigate the effect of mixing speed, water concentration, salt concentration, temperature as well as the various mechanisms in stabilizing the water-in-crude oil emulsions.

**MATERIALS AND METHODS**

**Materials:** Three crude oils were used in this study namely, Crude oil A from United Arab Emirates, UAE, Crude oil B from Kuwait oilfields and Crude oil C from Malaysia oilfields. All three crude oils were obtained from Petronas refinery at Melaka. Their respective compositions are given in Table 1. A detailed procedure for the water-in-crude oil emulsions (w/o) preparation and their procedures including the formation of w/o emulsion, their characteristics and method of preparation are thoroughly described in a previous research paper by Abdurahman *et al.* (2006). Table 2 shows the composition of w/o emulsion formulations and their corresponding stabilities, while Table 3 shows the physical properties of the crude oils used. Here the work merely describes the main experimental steps. Water-in-crude oil emulsions were prepared by dispersing distilled water in crude oil at room temperature with a standard three blade propeller at speed of 1600 rpm. In order to prepare water-in-oil emulsion emulsions, the agent in oil methods was followed, which the emulsifying agent first dissolved in the continuous phase (oil), then water added gradually to the mixture (oil + emulsifying agent). The volume of the water settled to the bottom was read from the scale on the beaker with different times. The amount of water separation in percent was calculated as separation efficiency from the water observed in the beaker. The prepared emulsions were used to check for w/o or o/w emulsions. All emulsions investigated were type of water-in-oil emulsions (w/o).

**Determination of interfacial tension:** For the measurements of interfacial tension, a standard test method for surface and interfacial tension of solutions of surface active agents (ASTM) was used. The equipment used is Du Nouy Interfacial Tensiometer, equipped with 6 cm circumference platinum ring. Since oil is lighter than water, the aqueous solution (water) was first placed in the sample vessel and the ring was immersed therein. The oil on top of the water solution then oil was poured to form the two-layer system (emulsion). Contact between the oil and the ring was avoided during the operation. After following sufficient time (5 min) for the interfacial tension to come to its equilibrium value, measurements were taken.

**Determination of the Emulsions apparent dynamic viscosity:** The apparent dynamic viscosity for the prepared emulsions was determined by Brookfield

Table 1: Physico-chemical properties of crude oils, A, B and C

Crude oil	Crude oil A	Crude oil B	Crude oil C
Density ( $\text{g cm}^{-3}$ )	0.833	0.856	0.800
Viscosity (cp)	13.400	21.540	6.540
Surface tension ( $\text{m Nm}^{-1}$ ) at 30°C	24.670	26.840	22.780
Interfacial tension ( $\text{m Nm}^{-1}$ ) at 30°C	22.540	24.620	20.220

Table 2: Composition of W/O emulsion formulations and their corresponding stabilities

Emulsion	Stabilizer	Wt. % stabilizer in ext. phase (oil)	Emulsion type	Internal phase (%)
1	LSWR	0.50	w/o	50
2		0.75	w/o	55
3		2.00	w/o	60
4		5.00	w/o	70
5	Triton X-100	0.75	w/o	50
6		0.90	w/o	55
7		1.50	w/o	60
8		3.00	w/o	70
9	SDDS	1.00	w/o	65
10		1.50	w/o	70
11		3.00	w/o	75
12		3.50	w/o	80
13	Span 83	4.50	w/o	50
14		6.00	w/o	55
15		1.50	w/o	60
16		6.80	w/o	70

Table 3: Physical properties of crude oil used in the experiments

Crude oil	Density ( $\text{g cm}^{-3}$ )	Asphaltene (% w/w)	Resin (% w/w)	R/A ratio	Pour point
A	0.833	1.4	4.2	3	14
B	0.856	0.7	6.3	9	11
C	0.800	0.3	5.1	17	-15

Rotational Digital Viscometer Model LV/DV-III with UL adapter and spindles # 16 and 31. Brookfield Viscometer apparatus was equipped with a water bath thermostat.

**RESULTS AND DISCUSSION**

In the present investigation, the various factors affecting the stability and viscosity of three water-in crude oil emulsions stabilized by a non-ionic water soluble surfactant Triton-X-100 and an ionic surfactant sodium dodecyl sulphate SDDS, Low sulphur wax residue (LSWR) and Sorbitan monooleate (Span 83) were thoroughly studied. These factors are the oil content of the emulsion, the surfactant concentration, temperature, agitation speed and salinity of water.

**Effect of water content of the emulsion:** The first part of this study deals with the formation, production and stabilization of w/o emulsions, while in the second part discusses the emulsion breaking (demulsification) of w/o. Table 2 shows the composition of w/o emulsion formulations and their corresponding stabilities. The effect of water content of the emulsion on its stability,

processing time, dynamic shear viscosity, density and pour point was investigated. In this respect, the water content of the emulsion was varied from 30 to 70 vol % (for stability purpose) with respect to the total volume of the emulsion. LSWR and Triton X-100 water-in-oil (w/o) emulsions were made with 50, 55, 60 and 70% (v/v) internal phase (water). For the 50 and 55 emulsion, a higher solids concentration was found ( $6 \text{ mg mL}^{-1}$  oil versus  $2 \text{ mg mL}^{-1}$ ) allowed easier emulsification and slowed the settling process. The 60 and 70% emulsions were appeared fairly stable with little settling. The LSWR and Triton X-100 stabilized emulsions exhibited only slight coalescence over three days. Some globule formation was observed and settling occurred. In contrast, the Span 83 emulsions were different from LSWR and Triton X-100 emulsions, even at similar dispersed phase volume fractions. Emulsions were made at 50 and 55% (v/v) internal phase with surfactant concentrations in the oil phase of 1.5 and 4.5% (w/w), at 60% (v/v) (3% w/w) and at 70% (v/v) (6.8% w/w). The different between surfactant concentrations for the 50 and 55% emulsions made by Span 83 appeared very significant on emulsions stability. High Span 83 concentrations increased emulsion stability; therefore, for high concentration of Span 83, the viscosity of w/o emulsion increased considerably and the emulsion droplets lost their shape. The effect of the disperse phase on the stability of emulsion systems also examined with sodium dodecyl sulphate, (SDDS) as the emulsifying agent. In this regards, the SDDS emulsions were made with 65, 70, 75 and 80% (v/v) (1 to 3.5 w/w in oil) internal phase. An increase in the concentration of SDDS in oil did not cause an increase but decrease of demulsification rate. The decrease would be induced by the increase of the surface potential of water droplets arising from the increase of the density of SDDS anion on the surface, which overcame the decrease of the surface potential by the increase ionic concentration in oil.

The emulsion stability for crude oils A, B and C were examined as function of processing time and emulsifier applied (surfactant). Stability evaluated via the ratio of the total water separated. The evaluation was carried out with agitation speed at 1800 rpm at 30 min at 30°C. As demonstrated in Fig. 1 and 2, in most cases stability of emulsion increases with processing time.

It is worth noticing that all surfactants permit a very long time for separation of the water phase (emulsion more stable). However, the maximum amount of water separated from crude oil A was (50%) and Crude B was (60%), crude C was (67%). From these observations, the classification in terms of decreasing stability efficiency is therefore the following; SDDS > Triton X-100 > LSWR > Span 83, respectively.

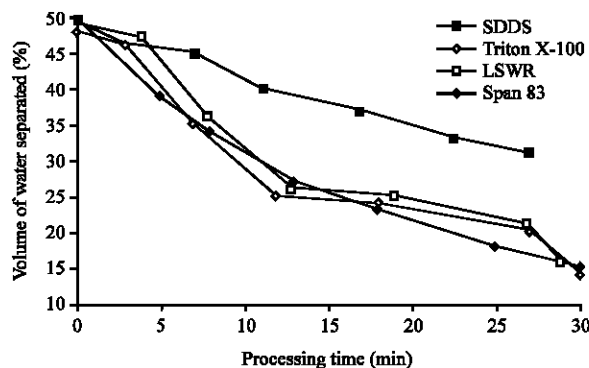


Fig. 1: Change of emulsion stability for Crude oil A emulsions (50-50% w/o), as function of processing time and emulsifier applied

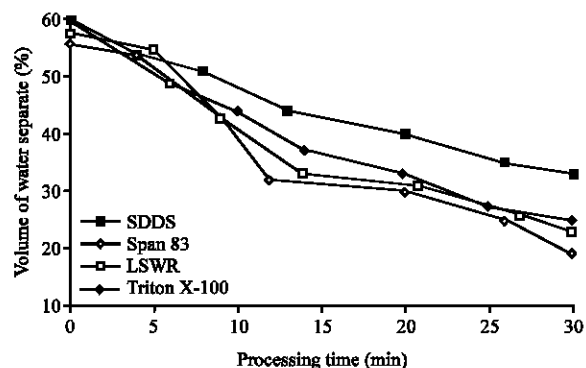


Fig. 2: Change of emulsion stability for Crude oil B emulsions (50-50% w/o), as function of processing time and emulsifier applied

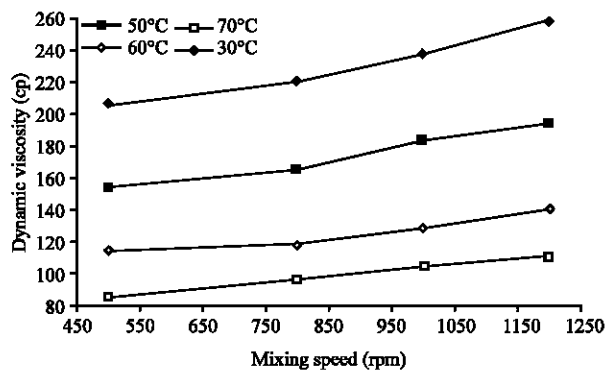


Fig. 3: Dynamic viscosity of the emulsion as a function of mixing speed

**Effect of the speed of mixing on the stability and viscosity of the emulsion:** The apparent dynamic viscosity of the crude oil emulsion (w/o) was investigated for the three crude oils for different mixing speeds at 30°C for 30 min. As shown in Fig. 3, which is a plot of apparent dynamic viscosity as a function of different mixing speed,

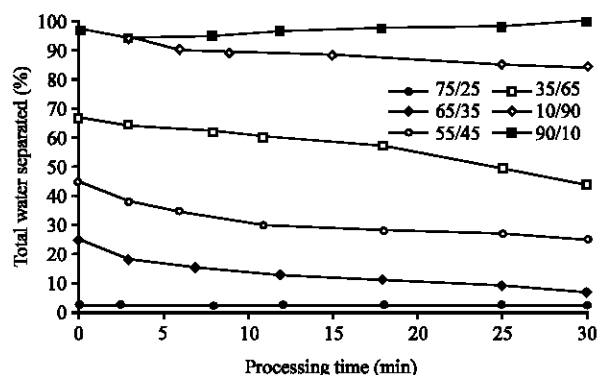


Fig. 4: Change of (w/o) emulsion stability for crude oil emulsions (stabilized with Span 83 surfactant) as function of processing time. Stability evaluated via the ratio of total water separated

it is clear from Fig. 3, there is a correlation between dynamic viscosity and mixing speed, which is; as increasing the mixing speed, result in increasing the viscosity of the emulsion.

Again to confirm the effect of stirring time and phase ratio on emulsion stability, water-in-crude oil with various volume ratios as shown in Fig. 4 was investigated. At low internal phase ratio water/oil (10-90%), only low stability was obtained, the increment of internal phase (water) continued till (75-25%). It's interesting to observe that, increasing the phase ratio, surfactant availability increases accordingly leading to highly stable emulsion. The variation in stability of the emulsions with phase ratio (75-25%) it is very difficult to explain its behavior especially during the first 8 min of the processing. When the volume of dispersed phase reached to (90-10%), the emulsion behavior completely has changed as shows in Fig. 4. The emulsion changed from w/o to o/w, from these measurements and observations, it can be deduced that the phase inversion point should be in the range of 68-72% water. As the volume of the dispersed phase increases, the continuous phase must spread out farther to cover all of the droplets, this causes the likelihood of impacts to increase, thus decreasing the stability of the emulsion. This means that, the emulsion might not break as increase the volume of the dispersed phase. In fact this increment caused an emulsion to invert from one phase (w/o) to another (o/w).

The influence of temperature on the rheologic behavior of the emulsions was investigated. The viscosity of the three crude oils were measured at the constant shear rate of  $400 \text{ sec}^{-1}$  over the temperature interval  $0-45^\circ\text{C}$ , using Brookfield Rotational Digital Viscometer Model LV/DV-III with UL adapter and spindles # 16 and 31 as shown in Fig. 5. The viscosities of the emulsions

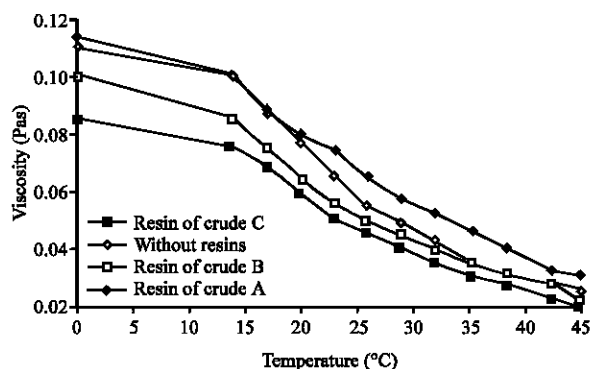


Fig. 5: Viscosity vs. temperature

proved to be nearly independent of the kind of the resins. It is remarkably, emulsion is very sensitive to temperature, as temperature increases, the viscosity decreases fast.

**Resin/asphaltene ratio:** The first step in determining the effect of the ratio of resin to asphaltene concentration on emulsion stability was preparation of crude oil emulsions and the percentage of resin and asphaltene in the crude oil. The presence of asphaltene and resin in crude oil can stabilize the emulsion. Asphaltene and resin act as an emulsifying agent, which reduce the interfacial tension and to induce repulsive forces between the droplets. Therefore, the resin/asphaltene ratio (R/A) is an important parameter to predict the emulsion stability. Resins increase the solubility of asphaltene in the crude and minimize the asphaltene interaction with water droplets. The resin/asphaltene ratio (R/A) may be expected to provide valuable information on tight emulsion formation. In this regards, the R/A ratio for crude oils A, B and C were found as 3, 9 and 17, respectively. The experimental results of this study shown that, crude oil C fractions which have higher R/A ratio (17) were separated easily than that of lower R/A ratio (Crude A and B). It may concluded that, when R/A ratio decreased, the emulsions are become tighter and harder to break. High resin concentration keeps more of the asphaltene dissolved in the oil phase. In this study, crude oil A was found more stable than crude B and C, respectively.

## CONCLUSIONS

The effect of the resin/asphaltene (R/A) ratio, surfactant concentration, water content, agitation speed and temperature on crude oil emulsion stability has been shown. High resin/asphaltene (R/A) ratios decrease the water-in-oil emulsion stability. The effectiveness of water-in-oil emulsion stabilization increases with increasing surfactant concentration and decreases with increasing temperature.

**REFERENCES**

- Abdurahman, H.N., M.Y. Rosli and Z.K. Jumaat, 2006. Study on demulsification of water-in-crude oil emulsions via microwave heating technology. *J. Applied Sci.*, 6: 2060-2066.
- Berger, P.D., C. Hsu and J.P. Arendell, 1987. Designing and selecting demulsifier for optimum field performance based on production fluid characteristics. *Soc. Pet. Eng. SPE-16285*, pp: 457.
- Brandvik, P.J. and P.S. Daling, 1991. W/O-emulsion formation and w/o emulsion stability testing-an extended study with eight oil types. DIWO Report No.10. IKU Sintef Group. Trondheim. Norway, pp: 48.
- Fingas, M., B. Fieldhouse and J. Mullin, 1994. Studies of water-in-oil emulsions and techniques to measure emulsion treating agents. In: *Proceedings of the Arctic Marine Oilspill Program Technical Seminar*. Environment Canada, Ottawa, Ontario, pp: 213-244.
- Kilpatrick, P.K. and J.D. McLean, 1997. Effects of asphaltene solvency on stability of water-in-crude oil emulsions. *J. Colloid Interface Sci.*, 189: 242.
- Krawczyk, M.A., D.T. Wasan and C.S. Shetty, 1991. Chemical demulsification of petroleum emulsions using oil-soluble demulsifiers. *Ind. Eng. Chem. Res.*, 30: 367.
- Mingyuan, L., A.A. Christy and J. Sjoblom, 1992. Emulsions-A Fundamental and Practical Approach. Sjoblom (Ed). Vol. 363, NATO ASI Ser, Kluwer Academic Publishers, pp: 157.
- Mohammed, R.A., A.I. Baily, P.F. Luckham and S.E. Taylor, 1993a. Dewatering of crude oil emulsions.1. Rheological Behavior of the Crude Oil-Water Interface. *Colloids Surf.*, 80: 222.
- Mohammed, R.A., A.I. Baily, P.F. Luckham and S.E. Taylor, 1993b. Dewatering of crude oil emulsions.2. Interfacial properties of the asphaltene constituents of crude oil. *Colloids Surf.*, 80: 237.
- Mohammed, R.A., A.I. Baily, P.F. Luckham and S.E. Taylor, 1993c. Dewatering of crude oil emulsions. 3. emulsion resolution by chemical means. *Colloids Surf.*, 83: 261.
- Mikula, R.J., 1992. Emulsion Characterization. In: *Emulsions Fundamentals and Applications in the Petroleum Industry*, Shramm, L.L. (Ed). *Advances in Chemistry Series 231*. Am. Chem. Soc., Washington, DC., pp: 79-129.
- Sjoblom, J., H. Hoiland, O. Urdah, A.A. Christy and E.J. Johansen, 1990a. Water-in-crude oil emulsions. Formation, characterization and destabilization. *Prog. Colloid Polym. Sci.*, 82: 131.
- Sjoblom, J., H. Sonderlund, S. Lindblad, E.J. Johansen and I.M. Skjarvo, 1990b. Water-in-crude oil emulsions from the Norwegian continental shelf. Part II. Chemical destabilization and interfacial tensions. *Colloid and Polymer Sci.*, 268: 389-398.
- Sjoblom, J., L. Mingyan, A.A. Christy and T. Gu, 1992. Water-in-crude oil emulsions from the Norwegian continental shelf. Part 7. Interfacial Pressure and Emulsion Stability. *Colloids Surf.*, 66: 55.
- Sjoblom, J., L. Mingyan, A.A. Christy and H.P. Ronningsen, 1995. Water-in-crude oil emulsions from the Norwegian continental shelf. Part 10. Aging of the interfacially active components and the influence on the emulsion stability. *Colloids Surf.*, 96: 261.
- Yan, Z., J.A.W. Elliott and J.H. Masliyah, 1999. Role of various bitumen components in the stability of water-in-diluted bitumen emulsions. *J. Colloid Interface Sci.*, 220: 329.
- Wasan, D.T. and A. Nikolov, 1993. Emulsion stability mechanisms. *Proceedings of the 1st World Congress on Emulsions*. Paris, France. Oct. 19-22, 4: 93.