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INVESTIGATING THE KINETICS OF WATER-IN-CRUDE OIL EMULSION STABILITY

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ABSTRACT

A problem of both fundamental and practical importance to the oil industry is water/oil (w/o) emulsions of which the stability is characterized by creaming or sedimentation, flocculation, coalescence of droplets, and/or phase separation. The knowledge and control of the destabilization mechanisms are crucial for an effective and efficient crude oil dehydration. The aim of this study is to investigate the effect of stability on the aging of w/o emulsions for proper characterization and resolution. Bottle test method is commonly used to determine the stability of emulsions in the oil and gas industry. However, the technique is tedious, time consuming and subjective. Thus, a more robust, accurate and automatic multiple light scattering technique was used to characterize several samples of w/o emulsions of varying water content and salinities. Analyses show that all samples exhibited similar stability behaviour as the original crude oil at ambient conditions. Increase in temperature to 70 ^{o}C led to little sedimentation in all the emulsions. The stability profiles clearly indicated that the emulsions are kinetically stable.

Keywords: emulsion stability, light-scattering, phase separation.

INTRODUCTION

Developing a technique for resolving water-in-crude oil emulsions involves adequate knowledge of the emulsion stability kinetics. Crude oil emulsions are colloidal dispersions of oil droplets in water (oil-in-water) or water droplets in oil (water-in-oil) which result from agitation encountered at the chokes, valves and other flow restrictions. Asphaltenes have been reported to stabilize water-in-oil emulsions by forming high-strength visco-elastic films around water droplets in the crude oil (Ekott & Akpabio, 2013), (Kokal, 2006), (Strassner, 1968). Besides, studies have also shown that resinous and aromatic molecules contribute to emulsion stability by accumulating at the oil-water interface. (Dicharry et al, 2006). When precipitated, other fine substances such as wax and naphthenic acids contribute to the emulsion stabilization (Meriem-Benziane and Zahloul, 2013). The importance of other components which may be present in the crude oil such as inorganic solids in emulsion stability has also been reported (McMahon, 1992).Water-in-crude oil emulsions have different classes of stability. Fingas and Fieldhouse, (2004) listed four classes of stability as stable, meso-stable, unstable, and entrained water. These four classes can be differentiated by visual appearance as well as by rheological measurements (Fingas and Fieldhouse, 2003). The sizes of the droplets could be in the micrometer and even submicrometer range (Petsev, 2004).

Derjaguin-Landau-Verwey-Overbeek (DLVO) theory has been used to analyze colloidal stability (Petsev, 2004). Contrary to the claim by DLVO theory that emulsion stability depends on the balance between van der waals attraction and electrostatic repulsion only, steric repulsion, depletion attraction, hydration and hydrophobic interactions, oscillatory surface forces have been identified as contributors (Claesson, et al, 2001), (Petev, 2004). Droplet fluidity, interfacial mobility and emulsifying agents may also have strong impact on the stability of emulsions (Sjöblom, *et al.*, 2002). Consequently, the droplets are prevented from rapid coalescence and emulsion is, thereby unable to resolve itself in a defined time period without some form of destabilization techniques.

All emulsions, perhaps with the exception of microemulsions, are thermodynamically unstable. The contribution of the interfacial free energy is proportional to the total area of contact between the two phases and is usually positive. Destroying the droplets and separating the phases macroscopically allows for considerable reduction of this unfavourable term, and therefore of the overall free energy (Wasan and Nikolov, 2001). The time scales on which such event occurs may vary from seconds to years. Hence, emulsions are usually kinetically stable. The life time of emulsions vary considerably from one system to another depending on the nature of the emulsifying agents, the nature of both phases and their volume ratio (Schmitt, et al, 2004). Oswald ripening and coalescence are two distinct mechanisms that lead to irreversible coarsening. The destruction scenario of emulsions result from the interplay between these two mechanisms.

However, predicting the destruction scenario and the emulsion lifetime still raise challenging questions. Knowledge of the basic principles and mechanisms governing emulsion stability presents both academic and applied interest. The analysis of emulsion stability provides not only fundamental challenges of great scientific interest, but is also very important for various practical aspects. Destabilization and separation of stable emulsions is a major concern during crude oil dehydration. Bottle tests are used to monitor the efficiency of additives on the de-emulsification of crude oil. They are easy to perform but can take a long time waiting for the full separation and are subject to the

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judgment of the experimenter who measures the thickness of the phases and in some cases their relative opacity. Bottle tests are a tedious and subjective exercise that is time consuming.

Subsequently, several experimental techniques have been developed and used to gain mechanistic understanding of both the structure and stability of emulsions. Wasan and Nikolov (2001) highlighted film rheometry for dynamic film properties, capillary force balance in conjuction with differential microinterferometry for drainage of curved emulsion films, back-light scattering for structure factor (Kossel diffraction), for structure factor, direct imaging for effective interdroplet interactions and piezo imaging spectroscopy for drop-homophase coalescence-rate processes. These methods lead to the determination of emulsion stability. The objective of this work is to use Turbiscan in the determining emulsion stability and monitoring the mechanisms of destabilization for effective prediction of the shelf-life of water-in-crude oil emulsions. Turbiscan consists of a scanning device and two detectors in transmission and backscattering. Detection of phase separation is quicker and much objective than visual observation as done in bottle test method. The opacity or transparency of the phases can be quantified optically and not left to human appreciation. Different samples can be easily compared via kinetics of phase separation.

MATERIALS AND METHOD

Materials

The crude oil sample used for this research was obtained from PETRONAS, Malaka. The properties of the crude oil are given in Table-1a. The interfacial tension (IFT) of the crude in fresh water and the prepared brine solutions was measured using spinning drop tensiometer (Table-1b). SARA content (Table-2) of the crude oil sample was determined using ASTM D3279 and D6591. Viscosity (ASTM D445) and density of the crude oil were measured at ambient pressure and temperature, 50 ºC and 70 ºC. Synthetic brines (20000ppm and 40000ppm) were prepared to simulate oilfield conditions.

Table-1a. Properties of the crude oil.

S/N	Temp (ºC)	Density (g/cm³)	API	Viscosity cP	Refractive index
1	25	0.9079	24.354	600.993	1.523
2	50	0.8909	27.328	174.326	1.511
3	70	0.8767	29.901	68.228	1.502

Table-1b. Interfacial tension of the crude oil.

S/N	Tempt (ºC)	IFT, mN/m		
		Zero salinity Water	Brine 20000ppm salinity	Brine 40000ppm salinity
1	50	13.9248	9.3770	11.6847
2	70	9.2829	5.3807	8.7446

Table-2. SARA content of the crude oil.

Asphaltene, %	Resin, %	Saturate, %	Aromatics, %
2.09	26.30	53.21	18.40

Emulsion preparation

Water-in-oil emulsions were prepared by mixing crude oil with fresh water and synthetic brine in turn (volume/volume). The two phases were homogenized using Hamilton constant mixer. No external emulsifier was applied since the aim was to achieve asphaltene-stabilized emulsions. The samples were agitated for five minutes to achieve stable emulsions. 100ml of emulsion was prepared at a time for uniformity and repeatability purpose. Electrical conductivity method was used to identify the nature of the emulsions. The crude oil and the emulsions were non-conductive while the electrical conductivities of fresh water and the brine solutions were measured as shown in Table-3. In water-in-oil emulsions, the fresh water and the brine solutions were dispersed and the droplets are encapsulated by the natural emulsifiers in the crude oil. The electrode of the conductivity meter can only make contact with the continuous phase and thereby giving the electrical conductivity of the crude oil as that of the emulsions. All the emulsions formed were water-in-oil.

Table-3. Electrical conductivity.

S/N	Material	Electrical conductivity, µS/cm
1	Crude oil	0
2	Fresh water	0.231
3	Brine solution 1 (20000ppm)	844
4	Brine solution 2 (40000ppm)	1665
5	All Emulsions formed	0

Stability measurement

Stability of the emulsions was determined by conducting bottle tests at ambient temperature, 50 ºC and 70 ºC for five days. Moreover, Turbiscan classic MA 2000 was used to monitor the rate of sedimentation, flocculation and coalescence to determine the degree of stability of each emulsion composition formed. The testing tube was filled with 10ml of emulsion and 10 acquisitions were made at room temperature. The autoscan was set to obtain a scan acquisition at every two minutes. Subsequently, the emulsions were heated at 70 ºC for six hours in a water bath and 10 acquisitions were also made at two minutes interval for comparison.

RESULTS AND DISCUSSIONS

Bottle tests gave no visible phase separation after the test period (five days). Opacity was the only justification possible from the bottle tests. Hence, the

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emulsions were considered stable. The opacity of the emulsions was confirmed by transmission signals recorded by Turbiscan. There was zero percent transmission for the entire column of the testing tube occupied by the emulsions. Back scattering profiles were then used for stability analysis. The testing tube is about 70mm long and particle concentration with respect to tube height was determined through back scattering. For analysis, the profiles were observed for demulsification phenomena at three different divisions of the tube (at the bottom, middle and top). Increase in the concentration of the dispersed phase towards the bottom with lesser particles at the top indicates sedimentation. The first profile (measured at 0.00 minute) was set as reference for subsequent profiles to observe the change in back scattering recorded over time.

The emulsion stability profiles are presented for water-in-crude oil emulsions formed with fresh water and brine solutions (20000ppm and 40000ppm) at 20%, 40% and 50% water cuts. The difference in stability profiles at 25 ºC and 70 ºC corresponds to higher sedimentation due to increased density difference between the dispersed phase and the continuous phase. The crude oil and all the emulsions shared this behavior. There was little or no movement of emulsion droplets at 25 ºC over the test period. The profiles overlap throughout the entire length of the testing tube. The few spikes observed at the floor of the tube might be due to the original solid particles such as asphaltenes present in the original crude oil used. Figure-1 shows the acquisition scan for the pure crude oil at 25ºC. It is therefore logical to state that no destabilization mechanism took place in the emulsions at 25 ºC since the original stability profile of the crude oil was maintained.

Figures-2 to 7 show the stability profiles for the emulsions with fresh water cuts. The concentration of the droplets at the bottom of the tube increased slightly at 70 ºC at the three water cuts. Figures-3, 5 and 7 show that sedimentation was only observed within 5mm height of the testing tube and progressed with water cut. However, there was no any other noticeable change above 5mm height and the profiles are similar to the ones obtained at 25 ºC.

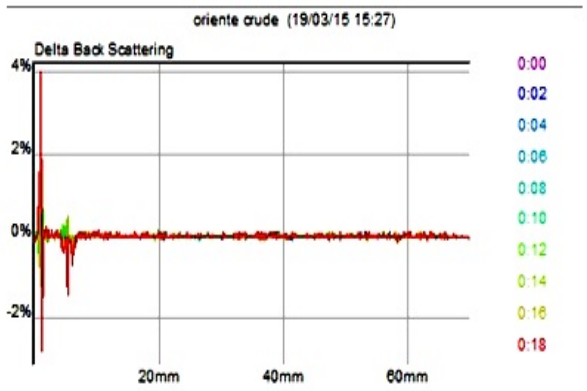

Figure-1. The stability profile of the original crude oil used.

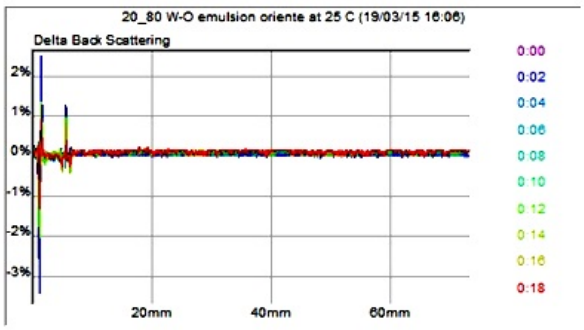

Figure-2. 20% Fresh water cut 25 ºC.

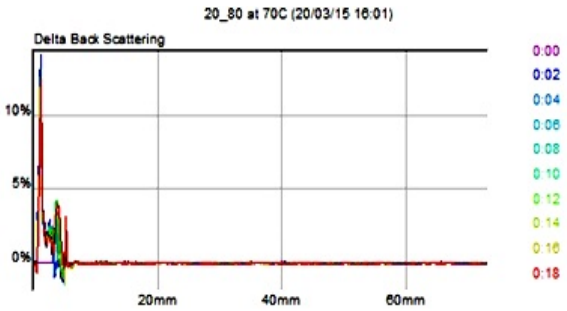

Figure-3. 20% Fresh water cut 70 ºC.

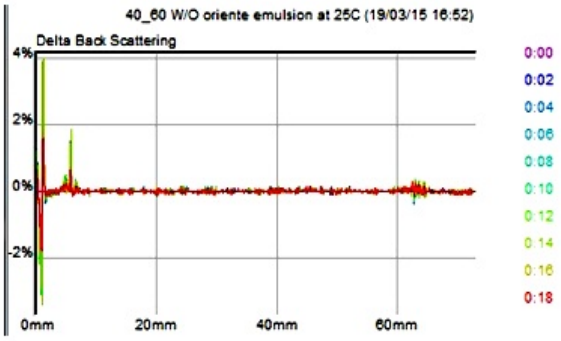

Figure-4. 40% Fresh water cut 25 ºC.

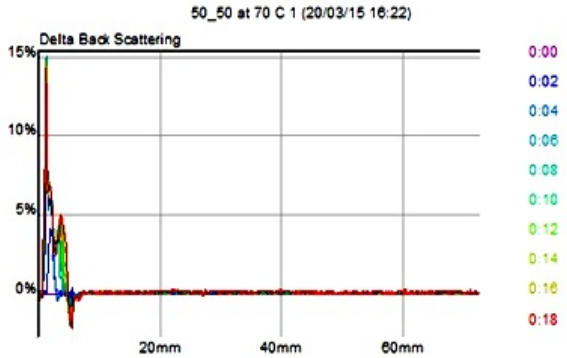

Figure-5. 40% Fresh water cut 25 ºC.

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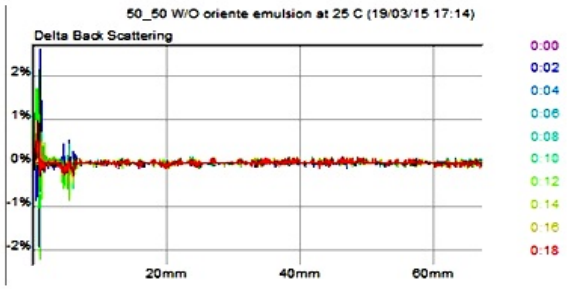

Figure-6. 50% Fresh water cut 25 ºC.

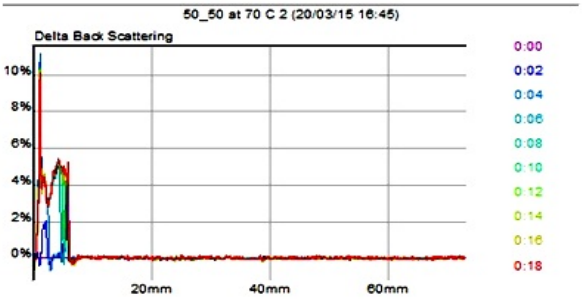

Figure-7. 50% Fresh water cut 70 ºC.

Figures-8 to 13 show that there was no much difference in the stability of the emulsions with increased salinity. The profiles assumed the same trend as those obtained in the fresh water cut emulsions. Despite the increase in density difference, the droplets are held in the bulk of the emulsions.

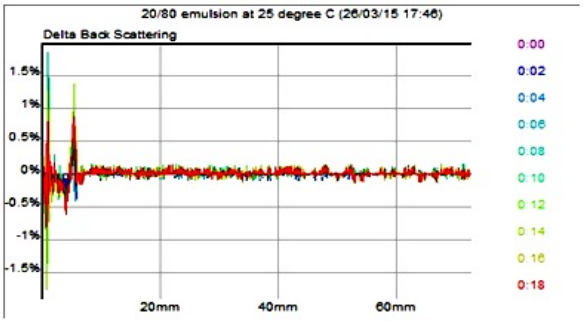

Figure-8. 20% water cut 25 ºC (20000 ppm brine solution).

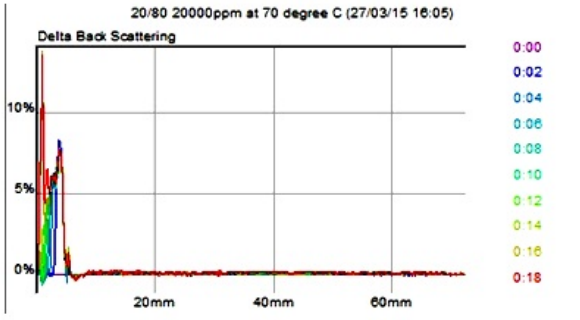

Figure-9. 20% water cut 70ºC (20000ppm brine solution).

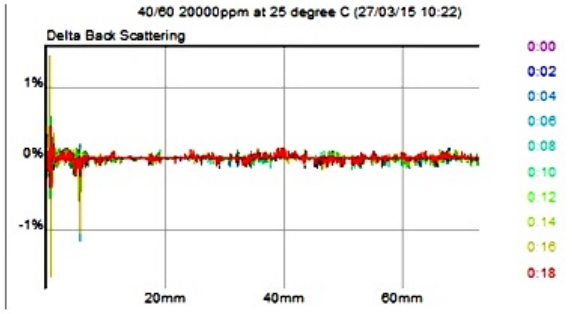

Figure-10. 40% water cut 25 ºC (20000 ppm brine solution).

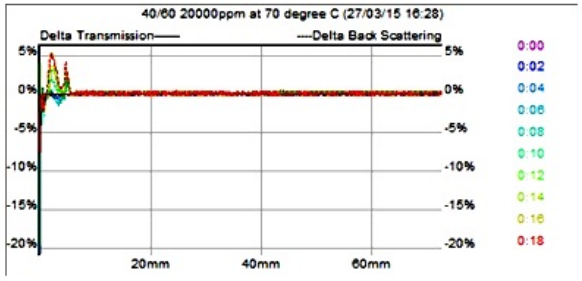

Figure-11. 40% water cut 70 ºC (20000 ppm brine solution).

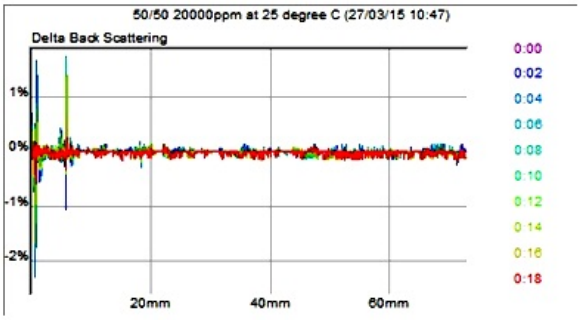

Figure-12. 50% water cut 25 ºC (20000 ppm brine solution).

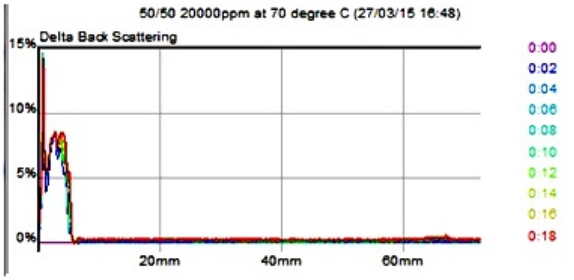

Figure-13. 50% water cut 70 ºC (20000 ppm brine solution).

Sedimentation was greater in the emulsion with 40% water cut at 70 ºC when the brine salinity was increased to 40000ppm (Figures-14 and 15). Both

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emulsions with 20% and 50% water contents maintained similar stability profiles with the emulsions with lesser saline dispersed phases as shown in Figures-16 to 19).

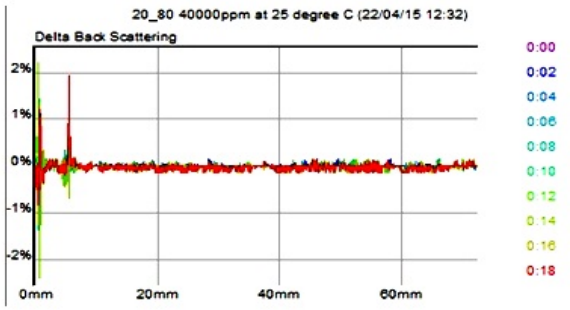

Figure-14. 20% water cut 25 ºC (40000 ppm brine solution).

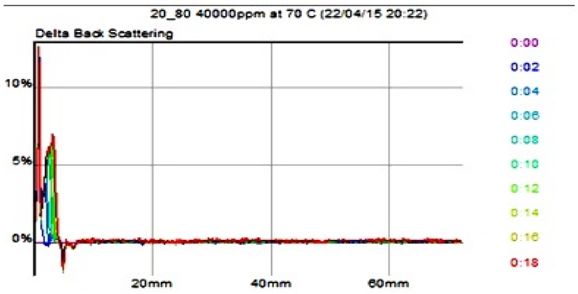

Figure-15. 20% water cut 70 ºC (40000 ppm brine solution).

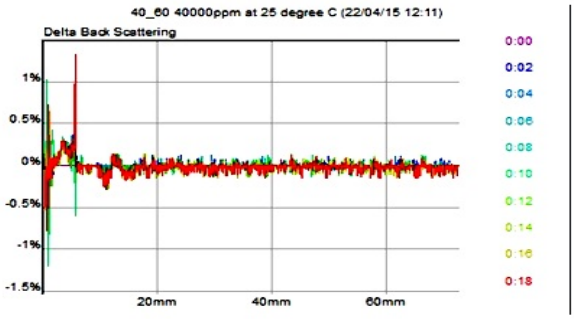

Figure-16. 40% water cut 25 ºC (40000 ppm brine solution).

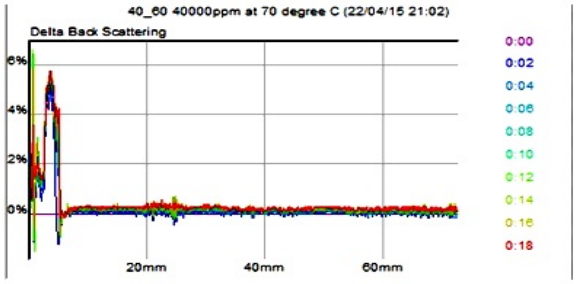

Figure-17. 40% water cut 70 ºC (40000 ppm brine solution).

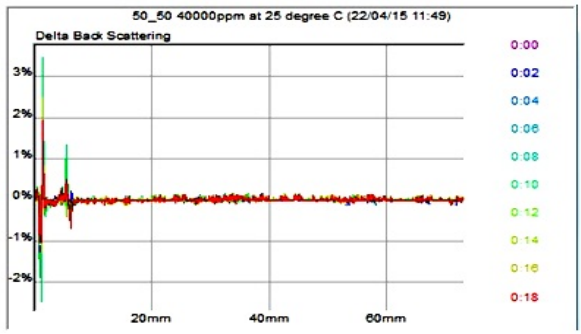

Figure-18. 50% water cut 25 ºC (40000 ppm brine solution).

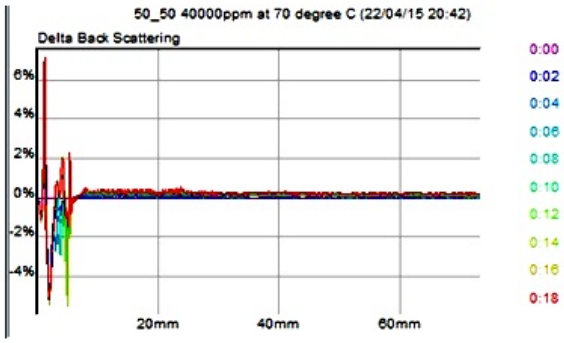

Figure-19. 20% water cut 70 ºC (40000 ppm brine solution).

Notwithstanding their thermodynamic instability, all the emulsions were kinetically stable and did not change appreciably for a prolonged period. These systems existed in the metastable state, that is, the potential barrier preventing aggregation of the particles was sufficiently high. To understand the reasons for the relative stability of the systems, it was necessary to first determine the stability and mechanisms of destabilization. Sedimentation stability distinguished the stability of the disperse phase with respect to enhanced force of gravity through reduced continuous phase viscosity. Phase separation due to sedimentation is a typical phenomenon for droplets in coarsely dispersed emulsions resulting in settling of the droplets.

The emulsions were kinetically stable since the droplets remained highly dispersed. They were characterized by diffusion–sedimentation subsequent equilibrium. Isothermal distillation of finer droplets in coarser ones caused subsequent sedimentation. Forces of molecular attraction may result in the formation of a continuously structured system with phase stability. There was no observed flocculation which is a process of particle cohesion. Flocculation might lead to formation of larger aggregates with a loss of sedimentation and phase stability and the subsequent phase separation, that is, a destruction of the emulsion. Hence, aggregative stability was observed due to the ability of the emulsions to retain the dispersion and individuality of the droplets. In aggregates, notwithstanding the change of their mobility, the droplets

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still remained as such for a certain time (possibly "lifetime") after which they can merge spontaneously with diminishing phase interface if destabilization techniques are applied. The Coalescence, that is, merging of droplets never occurred in any of the emulsions tested.

CONCLUSIONS

The stability of water-in-crude oil emulsions with different water cuts and dispersed phase salinities (0, 20000ppm and 40000ppm) was determined using both bottle tests and Turbiscan. Opacity was the only observation possible to ascertain the emulsion stability from the bottle tests. However, Turbiscan measurements gave adequate information about both the opacity and the kinetics of stability of the emulsions. The emulsions at room temperature exhibited the same stability profiles as the original crude oil. Increase in temperature to 70 ^{o}C led to little sedimentation in all the emulsions. There was no other mechanism of destabilization observed at increased salinity and water cuts. Therefore, destabilization may not occur for a long time (possibly lifetime) unless demulsification techniques are applied. The stability profiles from Turbiscan clearly showed that the emulsions were kinetically stable and their shelf life could be predicted. The properties of the demulsifiers such as molecular weight, needed to destabilize the emulsions could also be determined through the profiles. Finally, it was possible to compare the stability of various emulsions.

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