IJCPE
Iraqi Journal of Chemical and Petroleum Engineering

Iraqi Journal of Chemical and Petroleum Engineering
Vol.17 No.2 (June 2016) 37- 45
ISSN: 1997-4884

University of Baghdad
College of Engineering

The Effect of Asphaltene on the Stability of Iraqi Water in Crude Oil Emulsions

Sawsan A.M. Mohammed and Sally D. Maan
Chemical Engineering Department – College of Engineering – University of Baghdad

Abstract

In the present work, asphaltenes and resins separated from emulsion samples collected from two Iraqi oil wells, Nafut Kana (Nk) and Basrah were used to study the emulsion stability. The effect of oil resins to asphaltene (R/A) ratio, pH of the aqueous phase, addition of paraffinic solvent (n-heptane), aromatic solvent (toluene), and blend of both (heptol) in various proportions on the stability of emulsions had been investigated. The conditions of experiments were specified as an agitation speed of 1000 rpm for 30 minutes, heating at 50 °C, and water content of 30%. The results showed that as the R/A ratio increases, the emulsion will be unstable and the amount of water separated from emulsion increases. It was noticed that the emulsion of Nk crude oil became more stable at basic pH range, and reached to completely stabilized emulsion at pH=12. Whereas Basrah emulsion was stable in both acidic and basic pH ranges. Results indicated that toluene gave a good solubility for asphaltene, and a higher water separation for both crude oil emulsions.

A mathematical model to determine the kinetic constants that characterize the coalescence in the emulsions was also developed.

Key Words: crude oil, w/o emulsion, R/A, asphaltene solvency

Introduction

Water is usually present in crude oil reservoirs or injected as steam to stimulate oil production. Water and oil can mix while rising through the well and when going through valves and pumps to form in most cases relatively stable dispersions of water droplets in crude oil, which are usually referred to as oil field emulsions. About 80% of exploit crude oils exist in an emulsion state all over the world [1]. Water- in-oil emulsions are commonly encountered in the petroleum industry, such as in transportation stations dealing with crude oil and natural gas through pipelines and in petroleum refineries. Emulsions can cause difficulties in crude oil transportation and storage as well as pipeline corrosion. Emulsions are undesirable because the volume of dispersed water occupies space in the pipelines and processing equipments and increases capital and operating costs. Moreover, the physical properties and characteristics of oil change significantly upon emulsification. The density of emulsion can increase for the emulsion.

The most significant change is observed in viscosity, which typically increases [2]. Crude oil emulsions contains polar compounds such as asphaltenes and resins that play the role of natural emulsifiers and low molecular weight fatty acids, naphthenic acids in addition to many types of fine solids (clay, crystallized waxes, etc.), therefore, these emulsions can be very stable. These materials help in the formation of resistant films at the crude oil/water interface [3]. Asphaltenes are high molecular weight solids which are insoluble in paraffinic solvents and soluble in aromatic solvents such as toluene and benzene [5-7]. Resins are soluble in aliphatic hydrocarbons with low molar mass such as n-heptane, and in aromatic solvents such as toluene and benzene and insoluble in ethyl acetate [8]. Both asphaltenes and resins correspond to the heavy fraction of crude oil composed of polar molecules. Their structure contains heteroatoms such as oxygen, nitrogen, and sulphur, and metals such as vanadium, nickel, and iron. However, asphaltenes have higher molar mass, aromaticity, greater quantity of heteroatoms and metals [8, 9].

Asphaltenes are flat sheets of condensed polyaromatic hydrocarbons linked together by ether, sulfide, and aliphatic chain groups. The edges of the sheets are alkyl chains. The polar parts of the asphaltene molecules interact with each other forming micelles or aggregates. As such, these micelles are very much polar. Resins are less polar, and made up of smaller molecules with one end being hydrophilic made up of functional groups and the other end hydrophobic made up of alkyl chains. In crude oils, the resins are attached to the asphaltene micelles at the polar end and the non-polar end of the resin interact with crude oil.

The resins solvate the asphaltene aggregates and keep them in colloidal suspension in the oil. The aromaticity of the oil also increases the solvency of the asphaltene aggregates. The colloidal aggregates can be interfacially active if the interaction of the asphaltene with the water interface is favored over interaction with resins and aromatics in the crude oil phase. It is proposed that asphaltenes stabilize W/O emulsion if they are near or above the asphaltene precipitation onset point. This is the point at which the asphaltene start to precipitate, caused by addition of an alkane such as n-heptane to the crude oil [10]. Adding resins to W/O emulsion containing asphaltenes may reduce, promote, or have no significant effect on the emulsion stability depending on resins to asphaltenes (R/A) ratio and type (polar character).

To the best of our knowledge there has been no reported study about the effect of resin to asphaltene ratio (R/A) on the stability of Iraqi crude oil emulsions.

Experimental Work

Materials

The present work was carried out on selected two types of crude oil (Nk, Basrah). The physical properties of these oils are listed in Table (1).

Table 1, Physical properties of crude oils

Property	NK Crude Oil	Basrah Crude Oil
Sp.Gr at 15.6 °C	0.8160	0.8702
API	41.9	31.1
Asphaltene (%wt)	0.08	2.45
Kin.Viscosity (Cst) at 10 °C	7.2	24.3
Sulfur content (%wt)	0.58	2.66
IBP °C	45	39

Experimental procedure

Measurement of the Asphaltene and Resin Content of Crude Oil

16 g of crude oil (Basrah,Nk) was weighed and 200 ml of n-pentane was added to the crude oil to precipitate the asphaltene and mixed well using the magnetic stirrer. The crude oil pentane mixture was covered and let to stand for at least 14 hr (normally this is sufficient time for flocculation).The mixture was then filtered using vacuum. The flask was rinsed 2-3 times with 20 ml of pentane solvent each time and filtering was continued at steady rate. The precipitate was washed with fresh solvent until washing are colorless .The precipitate (asphaltene) was dried in an oven at 100 °C over night. The asphaltene was weighed to find the asphaltene content from the following equation:

$$asphltene\ content(\%) = \frac{weight\ of\ dried\ asphaltene\ (g)}{crude\ oil\ \ volume\ (ml)} \times 100 \quad \dots (1)$$

The n-pentane filtrate containing deasphalted oil (maltene) was collected. The filtrate was concentrated by heating (not higher than 50 °C).The adsorbent (silica gel) was prepared for adsorption work, and mixed well with the deasphalted oil until a viscous mass was formed (18g). The mixture (de-asphalted oil +silica gel) was transferred into a soxhelt extractor. (110 ml) n-pentane was added to the round bottom flask. The temperature was maintained at 40°C. Extraction was conducted with n-pentane in a soxhlet extractor. Extraction was continued by circulating until the liquid exiting the adsorbent bed is colorless (resembles the color of n-pentane solvent). The less polar materials (saturate and aromatic) are separated from the mixture. The solvent was replaced with chloroform and extracted again at 65 °C. Extraction was stopped when the liquid exiting the adsorbent bed was colorless (resembles the color of chloroform solvent). Chloroform facilitates the desorption of resin from silica gel. The mixture was distilled at 65°C and dried at 60 °C, and obtained resin was weighed.

Emulsion preparation

The emulsions were prepared by adding 30% of water (pH=7) to the two samples of crude oil at room temperature. The emulsification was carried out by using a mixer at a speed of (1000 rpm) for 30 min to get good water in oil (W/O) emulsion. The emulsion was then heated to 50 °C by using a heating plate on magnetic stirrer. After heating, the emulsion was transferred into a 500 ml cylinder and allowed to settle under gravity for 24 hr, the amount of resolved water will be considered the most appropriate measure of emulsion stability.

To study the effect of changing resin to asphaltene ratio, emulsion samples of different weight ratios of resin to asphaltene were preperad by dissolving (0.2,0.4, 0.6 and 0.8g)of resins respectively in 10 ml toluene, then mixed with crude oil.

The same procedure was carried out to monitor the effect of the addition of surface active solvents on the emulsion stability. N-heptane, toluene, heptol 50 (50% n-heptane and 50% toluene) were added to the crude oil from 10% - 50% of the crude oil volume.

The change in pH value of aqueous phase was carried out by adjusting the pH of the water phase using hydrochloric acid (HCl) and sodium hydroxide (NaOH). The pH ranges used to study the effect of pH change on the stability of the emulsion were (2, 4, 9 and 12).

Another set of experiments were conducted to investigate the effect of demulsifiers Chimeic2439 and Rp968 on demulsification process. The doses of these demulsifiers were (20, 40, 60, 80 and 100 ppm), added to the emulsions under stirring, then heated to 50°C using a heating plate.

The final water separation percentage was calculated from:

$$seperate(\%) = \frac{seperated\ water\ volume}{inital\ water\ volume} \times 100 \qquad \ldots (2)$$

Results and Discussion

1- Separation of Asphaltenes and Resins from Crude Oil

Table (2) reports measurements of weight percent of asphaltenes and resins in crude oil samples, and resins to asphaltenes ratio(R/A). It can be seen from the table that Basrah crude oil has high weight percent of asphaltenes and low ratio of resins to asphaltenes, and this might cause high emulsion stability. Whereas, Nk crude oil has high ratio of resin to asphaltenes, this explains low emulsion stability.

Table 2, Asphaltenes and resins content in the used crude oils

Crude oil sample	Wt.% asphaltenes	Wt.% resins	R/A
Basrah	4.51	29.02	5.085
Nk	0.38	30.6	85.85

2- Stability of Emulsion

In this research the stability of emulsion was examined by measuring the droplet size distribution(DSD) for the two types of crude oil emulsions containing 30% water content using optical microscope (model N117M with fitted 5Mp Digital Camera, Beijing NOVEL Optics Co., Ltd/China).. The results are summarized in Table (3). It can be shown that Basrah crude oil emulsion has smaller droplet size diameter than Nk crude oil emulsion.

Table 3, Drop size distribution of emulsion droplet

Crude oil type	30% emulsion Droplet size (micron)
Nk	12.91-30.98
Basrah	10.33-20.8

3- Effect of Resins to Asphaltenes ratio (R/A)

The role of resins to ashpaltenes ratio in stabilizing emulsion was investigated by preparing emulsions of Nk and Basrah crude oils containing varying amounts of resins to asphaltenes ratio. Figure (1) and Figure (2) show the effect of adding resins extracted from Iraqi crude oils on W/O emulsion stability. It is clear that as the R/A ratio increases, the emulsion will be unstable and the amount of water separated from emulsion increases.

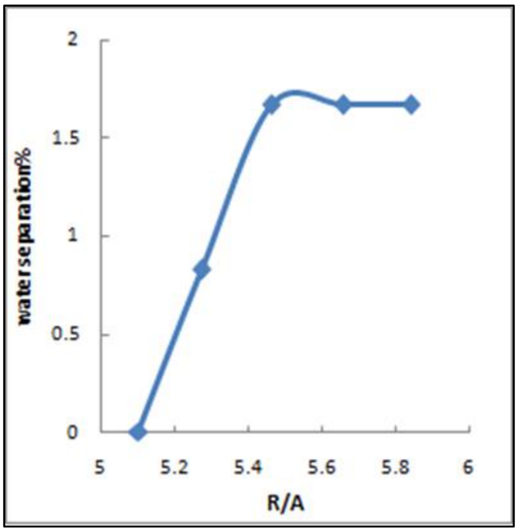

Fig. 1, Effect of R/A ratio of Basrah crude oil on emulsion stability

As it is noticed from Figure (1), Basrah crude oil formed stable emulsion and only very small amount of water was resolved. This could be related to the high percentage of asphaltene.

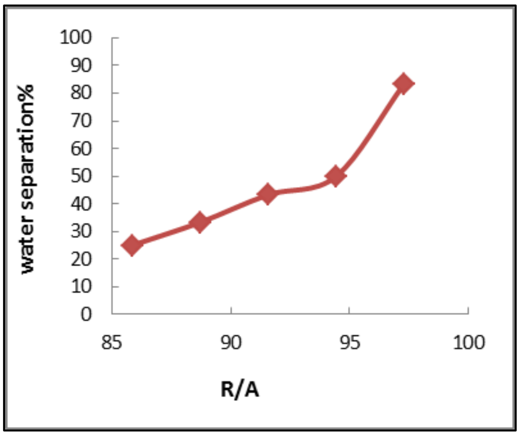

Fig. 2, Effect of R/A ratio of Nk crude oil on emulsion stability

For Nk crude oil, Figure (2) shows that increasing the resin to asphaltene ratio from 85.85 to 97.28 resulted in decreasing emulsion stability, and increasing amount of resolved water from (25-83%) respectively.

Addition of resins always destabilizes water-in-oil emulsion. It appears that resins act as a good solvent for asphaltenes, and at sufficiently higher concentrations are able to replace asphaltene at the water/oil interface that is likely more mobile and less likely to prevent coalescence. At very high R/A ratio, resins may act as a more competitive surface-active agent than as mediator of asphaltene adsorption [11].

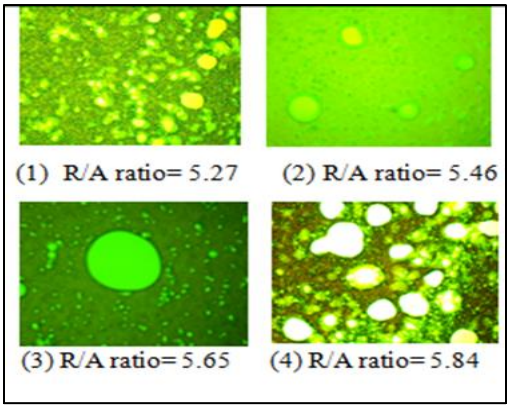

Fig. 3, Optical microscope images showing the droplet growth with increasing R/A of Basrah crude oil emulsion.

The droplet size after the addition of resins to both crude oils was measured by optical microscope as in Figures (3) and (4). The water droplets become larger with an increasing resin/asphaltene ratio, which means a decreasing in emulsion stability.

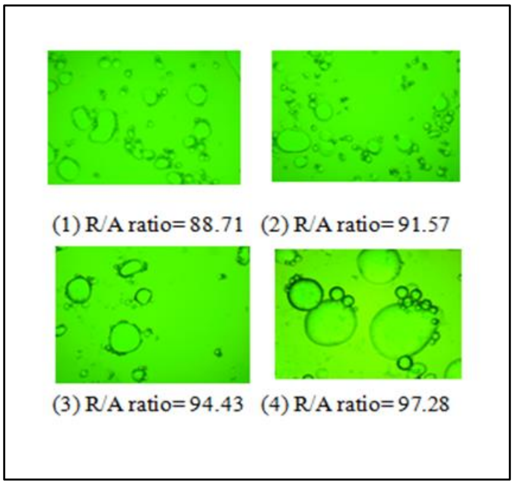

Fig. 4, Optical microscope images showing the droplet growth with increasing R/A of Nk crude oil emulsion

4- Effect of solvents addition on emulsion stability

It is known that asphaltene solvency is responsible for emulsion stability. The effect of changing the nature of the crude medium by blending the crude with solvents of varying amount of aromaticity was studied for the two types of crude oil.

In general, the effect of addition of the three solvents to the crude oils can be summarized as follows: for Basrah crude oil emulsion, it was observed that n-heptane addition did not resolve any water. While with toluene addition water resolved in fractions (20-50%) of toluene, and with heptol addition water resolved in fractions (30-50%) with lower percentage of water separated than that obtained from toluene addition as shown in Figure (5).

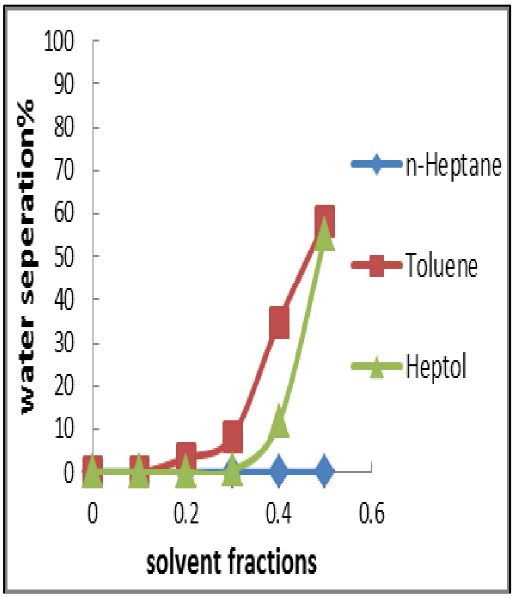

Fig. 5, Effect of added solvents on Basrah crude oil after 24 hr

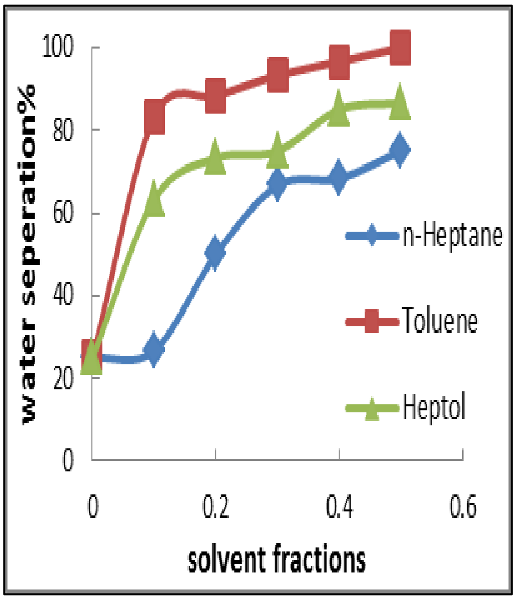

Fig. 6, Effect of added solvents on Nk crude oil after 24 hr

This means that Basrah crude oil has a higher tendency to form stable emulsion with water even when there are changes in the solvency of the asphaltene and resins in the crude.

This can be attributed to its low resin/asphaltene ratio of 5.085 and high asphaltene content of 4.51%.Whereas, Nk crude oil formed unstable emulsions when adding the three solvents as shown in Figure (6).

It was proved to be totally unstable due to addition of toluene; it gave away all the water used in the preparation of the emulsion at 50% of toluene addition to the crude oil sample.

It also gave away large amount of emulisified water due to the addition of heptol with 86.6% water separation on addition of 50% heptol to the crude oil sample.

For heptane addition, the water resolved is lower than that obtained for toluene and heptol addition, and the value of water separation is 75% on the addition of 50 % heptane.

This can be attributed to the high ratio of resin/asphaltene of 85.85 and low asphaltene content of 0.38%.

5- Effect of Aqueous phase pH

It could be concluded from Figure (7), that Basrah crude oil formed stable emulsion in the two ranges of pH (acidic and basic).

This is due to the strong interfacial film formed by asphaltene, whereas Nk crude oil formed unstable emulsion in acidic range of pH with maximum separation of 33.3% at pH =2 and did not resolve any water at basic range pH =12.

Crude oil emulsion contains polar fractions (asphaltenes and resins) at the interfacial film surrounding water droplets; these contain acidic and basic groups, therefore adding inorganic acid and base affect these films and their emulsion stability.

The interfacial films formed by asphaltenes are stronger in acid (low pH), intermediate in strength at natural pH and become very weak or mobile films in basic pH.

Whereas, the films formed by resin are stronger in base and weaker in acid medium [12].

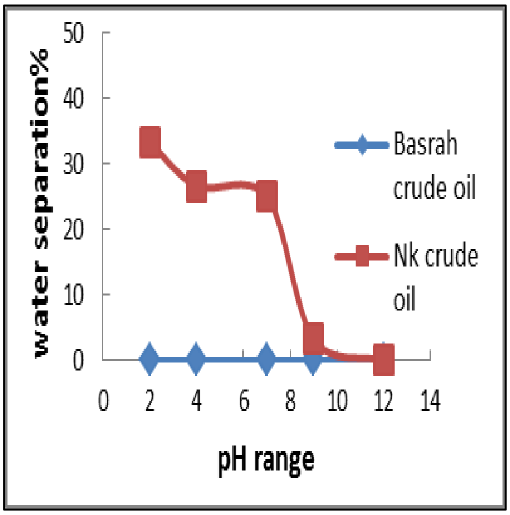

Fig. 7, Effect of pH on the two types of crude oil

Nk crude oil emulsion has high ratio of R/A, therefore the interfacial films are formed by resins; and this explain the behavior of Nk crude oil emulsion toward the change of pH.

6- Effect of Demulsifies Dose

Figures (8) and (9) show the effect of added demulisifers dose on the separation efficiency for the two crude oil emulsions.

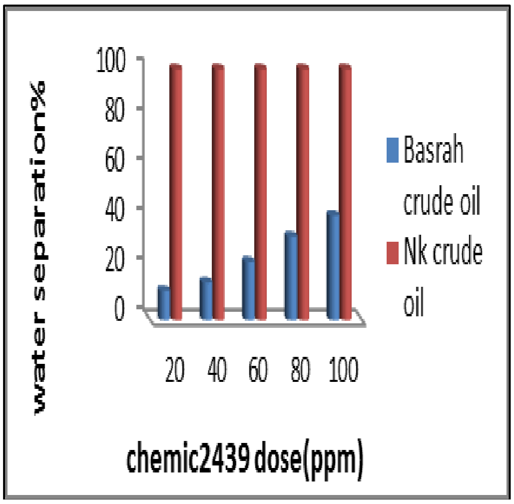

Fig. 8, Effect of chemic2439 dose on the demulsification of Basrah and Nk crude oil emulsions

It can be seen from Figures that complete separation for Nk crude oil emulsion was achieved for all doses of the two types of demulsifiers.

Whereas, for Basrah crude oil emulsion, the maximum water separation was 41.67% at (100ppm) chemic2439 and 66.67% at (100ppm) Rp968.

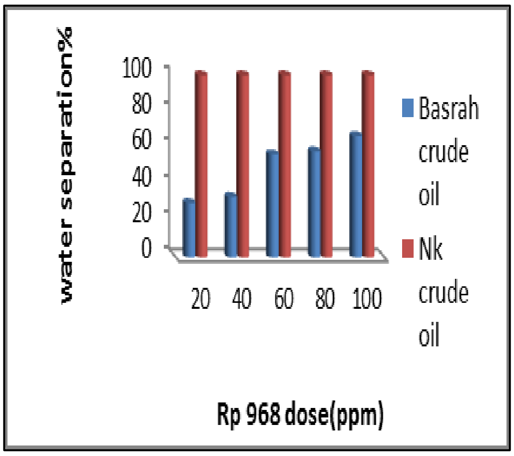

Fig.9, Effect of Rp968 dose on the demulsification of Basrah and Nk crude oil emulsions

Emulsion stability decreases as the concentration of the demulsifier increases up to a certain value. At this concentration, the demulsifier molecule performs a complete coverage of the water/oil interface dragging the asphaltene away from the interface. As a result, the protecting film present a round the dispersed water droplets thins, then it ruptures and coalescence occurs.

Kinetics of Emulsion Stability

The rate at which the emulsion water diminishes can be defined with a first order rate equation as:

$$\ln[\frac{CA\circ}{CA}] = k_c\, t \qquad \ldots (3)$$

Where:

C_{A0} Initial concentration of the water in the emulsion

C_A Concentration of the water in the emulsion at any time

t time(s)

A comparison of the stability of the two crude oil samples based on their breakage rate constant is carried out using the data of 50%addition of toluene in the crude oil samples as shown below in Figures (10) and (11).

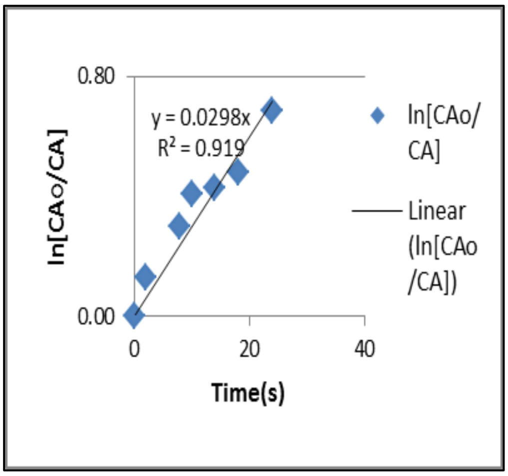

Fig. 10, Kinetic study for Nk crude at 50%addition of toluene

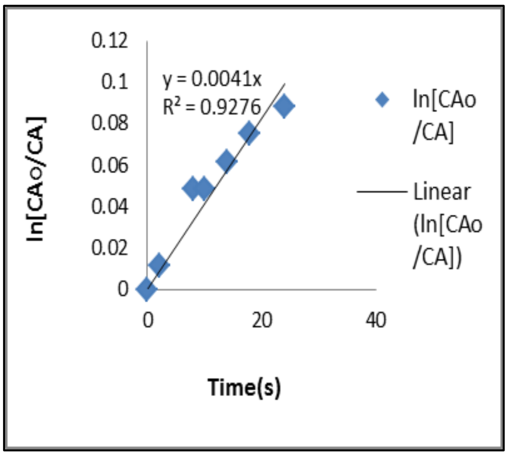

Fig. 11, Kinetic study for Basrah crude at 50%addition of toluene

From Figure (10) the breakage rate constant for Nk crude oil is k_c=0.029 s^{-1}, whereas for Basrah crude oil the breakage rate constant from Figure (11) is k_c= 0.004 s^{-1}. It can be seen that breakage rate constant for Basrah crude oil is far less than that of Nk crude oil when subjected to the same condition of solvent addition. This explains why Basrah crude oil forms a more stable emulsion than Nk crude oil.

Conclusions

1- Asphaltene percent in Basrah crude oil is 4.51%, whereas for Nk crude oil is 0.38%.
2- Nk crude oil emulsions have higher ratio of R/A than Basrah crude oil emulsions, therefore Nk emulsion has lower tendency to form stable emulsions.
3- For the same water content, Basrah crude oil emulsion has smaller droplet size diameter than Nk crude oil emulsion.
4- It is clear that as the R/A ratio increases, the looser the emulsion will be and the amount of water resolved from emulsion increases.
5- In general, the effect of addition of three solvents to the crude oils can be summarized as follows: for Basrah crude oil emulsion, it was observed that n-heptane addition did not resolve any water. While with toluene addition, higher percentage of separated water was obtained than from heptol addition. Nk crude oil formed unstable emulsions when adding the three solvents. It was proved to be totally unstable due to addition of toluene; it gave away all the water used in the preparation of the emulsion. It also gave away large amount of emulisified water due to the addition of heptol. For heptane addition, the water resolved is lower than that obtained for toluene and heptol addition.
6- Basrah crude oil formed stable emulsion in the two ranges of pH (acidic and basic). This is due to the strong interfacial film formed by asphaltene, whereas Nk crude oil formed unstable emulsion in acidic range of pH with maximum separation of 33.3% at pH =2 and did not resolve any water at basic range pH =12.
7- Complete separation for Nk crude oil emulsion was achieved for all doses of the two types of

demulsifiers. Whereas, for Basrah crude oil emulsion, the maximum water separation was 41.67% at (100ppm) chemic2439 and 66.67% at (100ppm) Rp968.

8- The process of emulsions coalescence can be defined with a first order rate equation with breakage rate constant values of 0.029 s^{-1} for Nk crude oil and 0.004 s^{-1} for Basrah crude using toluene as solvent.

References

1- Xia, L., Lu, S., Cao, G., 2004, “Stability and demulsification of emulsions stabilized by asphaltenes or resins’, Journal of Colloid and Interface Science, Vol.271, pp.504-506.

2- Fingas M. and Fieldhouse B. 2003, "Studies of Formation Process of water-in-Oil Emulsions", Marine Pollution Bulletin Vol.47, No. 9-12, pp.369-396.

3- Dalmazzone C., Noik C. and Clausse C., 2009," Application of DSC for Emulsified System Characterization" ,Oil & Gas Science and Technology - Rev. IFP , Vol.64, No. 5, pp.543-555

4- Ashoori, S., Abedini, A., Abedini, R., Qorbani Nasheghi, K.H., 2010,” Comparison of scaling equation with neural network model for prediction of asphaltene precipitation”, Journal of Petroleum Science and Engineering, Vol.72, pp.186-194.

5- Speight, J.G., Werrick, D.L., Gould, K.A., Overfield, R.E., Rao, B.M.L., Savage, D.W., 1985,”Molecular weight and association of asphaltenes: a critical review”, Revue de I’Institut Francais du Petrole, Vol.40, No. 1, pp.51-56.

6- Abedini, A., Ashoori, S., Torabi, F., Saki, Y., Dinarvand, N., 2011,”Mechanism of the reversibility of asphaltene precipitation in crude oil”, Journal of Petroleum Science and Engineering, Vol.78, pp.316-320.

7- Eskin, D., Ratulowski, J., Akbarzadeh, K., Pan, S., 2011,”Modelling asphaltene deposition in turbulent pipeline flows”, The Canadian Journal of Chemical Engineering, Vol.89, pp.421-441.

8- Aguilar, J.I.S., Neto, J.S.G., Almeida, S.M., Mansur, C.R.E., 2013,”Evaluation of the influence of polyoxidebased surfactants on the separation process of model emulsions of asphaltenes using the FTIR-ATR technique”, Journal of Applied Polymer Science, Vol.128, pp.1390-1397.

9- Mullins O. C., Groenzin H., Buch L., Gonzalez E. B., Andersen S. I., Galeana C. L., 2003,”Molecular size of asphaltene fractions obtained from residuum hydrotreatment”, Fuel, Vol.82, pp.1075-1084.

10- Gafonova, O.V. and Yarranton, H.W., 2001,”The stabilization of water-in-hydrocarbon emulsions by asphaltenes and resins”, J. colloidal interface Sci. Vol.241, pp.469-478.

11- Al-Sahhaf T., Elsharkawy A. & Fahim M. 2008,“Stability of Water-in-Crude Oil Emulsions: Effect of Oil Aromaticity, Resins to Asphaltene Ratio, and pH of Water”, Petroleum Science and Technology, Vol.26, No.17, pp.2009-2022.

12- Strassner, J.E. 1968, "Effect of pH on Interfacial Films and Stability of Crude Oil-Water Emulsions", J Pet Technol Vol.20, No.3, pp.303-312.