Journal of Applied Sciences

ISSN 1812-5654

science alert

ANSInet
an open access publisher
http://ansinet.com

Journal of Applied Sciences 14 (10): 1049-1054, 2014
ISSN 1812-5654 / DOI: 10.3923/jas.2014.1049.1054

Mechanism of Surfactant in Microemulsion Phase Behaviour

Khaled A. Elraies and Shehzad-Ahmed
Faculty of Geoscience and Petroleum Engineering, Universiti Teknologi PETRONAS,
Bandar Seri Iskandar, Tronoh, 31750, Perak, Malaysia

Abstract: This study presents the behavior of surfactant in microemulsion during chemical EOR process. Previous work performed on microemulsion phase behavior illustrated type III as the most suitable for achieving ultra low Interfacial Tension, assuming all surfactants to be soluble within the middle phase microemulsion. Based on our experimental results, this assumption was proven to be invalid. Phase behavior experiments were conducted at various salinity increments to generate gel and liquid crystal free microemulsion using surfactant and co-solvent. Different phases of type III microemulsion were then separated and analyzed for the surfactant partition distribution in the aqueous and microemulsion phase. The surfactant concentration in each phase was monitored by UV-visible spectroscopy. Observations from experimental results indicated that more than 31% of total surfactant was left behind in the aqueous phase rather than going entirely into microemulsion phase. Hence, the general statement that assumes all surfactant to be soluble in the microemulsion phase is not valid for all cases.

Key words: Surfactant, microemulsion phase behavior, UV-visible spectroscopy, type III microemulsion

INTRODUCTION

Capillary forces present in the reservoir are responsible for entrapping a large amount of oil during water flooding of petroleum reservoir. These forces conclude that IFT at the crude oil and brine interface plays a dominant role. The ultra low IFT can be achieved by surfactant flooding, but hurdle in the implementation of this method is the high cost of chemicals. Although recent research has improved its cost but still designing of efficient chemical formulation which is technically and economically suitable is the need of time.

Aqueous, oil and surfactant at certain condition produces micromeulsions (Lake, 1989; Green and Willhite, 1998). A microemulsion is a thermodynamically stable dispersion of oil and water which contains substantial amounts of both oil and water stabilized by surfactant. The IFT between microemulsion and excess phase can be extremely low (Green and Willhite, 1998; Flaaten *et al*., 2008; Sheng, 2010). Winsor (1954) characterized the microemulsion as being of three Types i.e., type I (lower phase), type II (upper phase) and type III (middle phase). Type I also known as oil in water microemulsion forms at low salinity by the solublization of some amount of oil in aqueous phase. Type II is water in oil microemulsion forms at high salinity by solubilizatoin of some amount of water in oil (Healy *et al*., 1976; Flaaten *et al*., 2010). At intermediate optimal salinity type-III microemulsion begins to form which has been found quit suitable for reducing ROS due to its unique properties i.e., ultralow IFT, large interfacial area, thermodynamic stability and the ability to solubilize both oil and water (Healy *et al*., 1976; Nelson and Pope, 1978; Pope *et al*., 1982; Flaaten *et al*., 2008).

Healy *et al*. (1976) first defined the water and oil solublization ratios as the ratio of either the volume of water (V_w) or oil (V_o) over the volume of surfactant (V_s). The solubilization ratio of oil i.e.:

$$\frac{V_0}{V_s}$$

increases with the increase of salinity, where as water solublization ratio i.e.:

$$\frac{V_w}{V_s}$$

decreases with the increase of salinity. The intersection point of oil and water solublization ratio verses salinity gives the optimal salinity (S↑* and optimal solublization ratio (σ↑* at which Type III microemulsion forms. All the surfactant was assumed to partition into the microemulsion phase (Healy *et al*., 1976; Aoudia *et al*., 1995; Zhao *et al*., 2008; Flaaten *et al*., 2010; Hirasaki *et al*.,

Corresponding Author: Khaled A. Elraies, Faculty of Geoscience and Petroleum Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, Tronoh, 31750, Perak, Malaysia

2011). Huh (1979) then derived a relationship b/w IFT and optimal solubilization ratio as Eq. 1 (Flaaten *et al*., 2008; Zhao *et al*., 2008; Hirasaki *et al*., 2011):

$$\gamma = \frac{C}{(\sigma^*)^2} \quad (1)$$

where, γ is interfacial tension, σ^* is optimal solublization ratio and C around 0.3 dynes cm^{-1}.

Salinity is important factor responsible for phase transition from type I to III to II. Addition of salinity neutralizes the electrical repulsive forces between micelles of anionic surfactant which cause them to aggregate and transformation of microemulsion from lower to upper phase i.e., (from type I to II) takes place (Chan and Shah, 1979; Kumar and Mittal, 1999). Salinity greater than optimal begins to low oil-microemulsion IFT to trap surfactant in residual oil (i.e., surfactant loss) and increases water-microemulsion IFT which reduces oil mobilization. Whereas salinity lower than optimal keeps the surfactant in aqueous phase, reduces water-microemulsion IFT and increase oil- microemulsion IFT which tends to reduce oil mobilization (Nelson and Pope, 1978; Chan and Shah, 1979; Pope *et al*., 1982; Levitt *et al*., 2006). Recovery efficiency in surfactant EOR highly depends on the degree of surfactant retention. Surfactant retention reduces concentration of surfactant in the injected surfactant slug and results in less oil recovery. Loss of surfactant in the reservoir takes place due to several mechanisms such as surfactant adsorption, precipitation, degradation and partitioning (Donaldson *et al*., 1989).

Up till now it was considered that in type III microemulsion all the surfactant is concentrated in the middle phase microemulsion which is not true. As surfactants have known interactions with oil and water, it is pertinent to assume that not entire surfactant molecules take part in the formation of middle phase microemulsion and distributes among aqueous, hydrocarbon and microemulsion phase. This distribution of surfactant between different phases of type III microemulsion is unfavorable for achieving ultra low IFT and lowers recovery efficiency with high surfactant loss in the formation either due to adsorption or retention. This study ascertains surfactant concentration in the aqueous phase of Type III microemulsion, prepared by using high performance commercial surfactant i.e., alcohol alkoxy sulfate with light crude.

MATERIALS AND METHODS

Obtaining optimal formulation can be experimentally time consuming, therefore a design methodology was adapted in which surfactant concentration and co-solvent concentration were varied. This methodology has efficiently evaluated chemicals and their interactions with each other and crude oil. A series of phase behavior experiments was performed and performance evaluation was made by comparing microemulsion parameters i.e., optimal solubilization ratio, optimal salinity and coalescence time. Chemical formulations having highest solubilization ratio and fast equilibrium time were selected. Surfactant distribution between micromeulsion and aqueous phase was analyzed with the help of UV-visible spectrophotometer. Steps followed in this study are as follows.

Materials description: A commercial good performance anionic surfactant i.e., Alcohol Alkoxy Sulfate (AAS), a cosolvent i.e., Secondary Butyl Alcohol (SBA) and an electrolyte i.e., NaCl were used in this phase behavior experiments to obtain the desired microemulsion. All phase behavior experiments were performed at 60°C with light crude.

Apparatus used in this experimental study includes borosilicate pipettes, pipettes stand, weighting balance, flame torch and UV visible spectrophotometer. Syringe connected to long needle was used to extract the aqueous phase of microemulsion and then UV visible spectrophotometer was used to measure the concentration of surfactant in the extracted aqueous phase.

Phase behavior experiments: Chemical mixtures containing surfactant, co-solvent and brine were tested and optimized in phase behavior experiments. Each phase behavior experiment used an array of pipette with incremental electrolyte differences to obtain microemulsion data versus electrolyte concentration. Aqueous phases prepared for phase behavior experiments contain surfactant, co-solvent and electrolyte. Equal volume of aqueous phase and oil phase were added in pipettes and pipettes were heated-sealed, cooled and slowly inverted several times to allow oil and aqueous phase mixing and then allowed it to settle for few hours or days till equilibrium time. The fluids in the phase behavior array were visually inspected and the salinity is recorded where cloudiness and/or phase separation occurs. Prior to the addition of crude oil in the pipettes, an aqueous stability assessment was conducted to determine the clarity and homogeneity of all aqueous phases. It has indicated the compatibility of surfactants with electrolytes in order to avoid phase separation or precipitation. Only those mixtures were selected for phase behavior studies which were found stable in experimental condition. After identifying the workable salinity range for each formulation, phase behavior experiments were performed

using finer salinity increments to obtain clear picture of all microemulsion types. Oil and water solubilization ratios were calculated and plotted verses salinity in order to obtain optimal salinity and optimal solubilzation ratio.

Chemical components i.e., surfactant, co-solvent and electrolyte were used in combination for optimal performance. Different formulations were tested by changing surfactant concentration and co-solvent concentration in order to achieve optimum formulation. Change of performance of microemulsion at different total surfactant concentration was noted from the shift of optimal point of solubilization curves. Equilibrium time of Type III microemulsions was recorded by noting volume change time to time. Concentration of surfactant and cosolvent fulfilling our requirements (i.e., high optimal solubilization ratio, less equilibrium time and low visocosity microemulsion) were selected.

Aqueous phases extraction and surfactant concentration determination: After identifying type-III salinity region, phase behavior experiments were performed with finer increment. Aqueous phases from the type III microemulsion were separated carefully by using syringe having long needle. Concentration of surfactant was measured after equilibrium with the help of UV visible spectroscopy technique. This technique was selected because of its high sensitivity and found suitable for detecting alcohol alkoxy sulfate surfactant. UV spectrophotometer gives absorption at different wavelength which is directly related to concentration. A straight line calibration curve was obtained by plotting known surfactant concentration verses absorption at 208 nm. NaCl present in the sample disturbs absorbance at 208 nm. NaCl was taken in the baseline in order to remove its effect on UV-visible absorption spectrum. Extracted aqueous phases were than diluted to bring their absorption within detectable range of UV-visible spectrophotometer and by using calibration curve, concentration of surfactant was measured.

RESULTS AND DISCUSSION

Phase behavior experiments: Number of Phase behavior experiments was performed by changing surfactant and co-solvent concentration for achieving Type III microemulsion. Commercial surfactant i.e., Alcohol alkoxy sulfate with concentration ranging from 1-4 wt.% were used in phase behavior experiments. Alcohol alkoxy sulfate has shown high solublization ratio with light crude which is indicator of achieving low IFT. This favorable solubilization ratio is because of PO groups present in the AAS surfactants and due to matching of surfactant chain length with crude oil (Leung and Shah, 1987). Oil and water solublization curves of two different formulation containing 2 and 4 wt.% surfactant at 6 wt.% cosolvent were plotted and shown in Fig. 1a and b. Solubilization ratio was found high at higher surfactant concentration and vice versa (Flaaten *et al*., 2008). Phase behavior experiments performed at low cosolvent concentration has shown cloudiness and viscous phases in the pipettes. When the concentration of cosolvent was increased to 6 wt.%, cloudiness disappeared and clear microemulsion having low viscosity was obtained (Sheng, 2010). Phase behavior pipettes of type III microemulsions achieved by two different surfactant formulation (i.e., 2 and 4 wt.%) at same cosolvent concentration (i.e., 6 wt.%) are shown in Fig. 2a and b. By comparing Fig. 2a and b, it is clear that microemulsion volume is high in case of 4 wt.% surfactant. This shows that microemulsion volume is directly related to surfactant concentration (Green and Willhite, 1998).

Type III microemulsion phase volume and equilibrium time: Volumes of Type III microemulsions at various

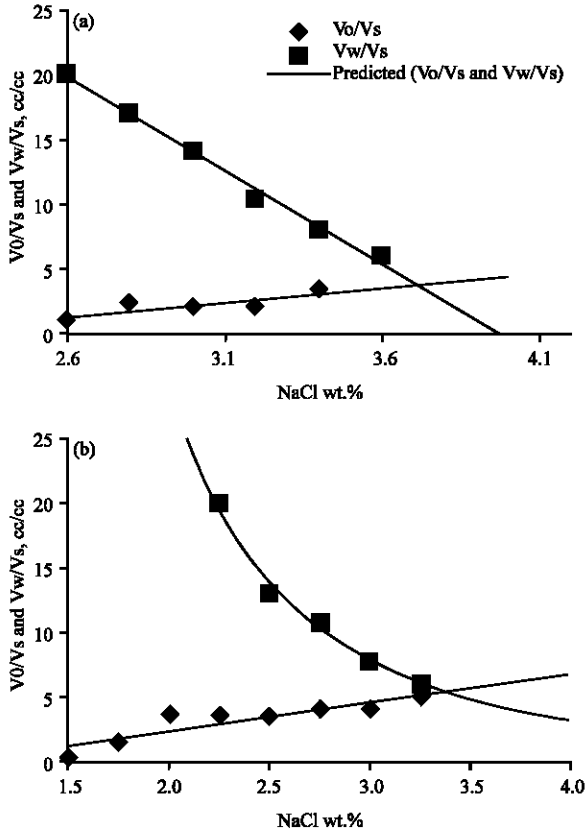

Fig. 1(a-b): Oil and water solubilization ratio vs. salinity for (a) 2 wt.% surfactant and 6 wt.% cosolvent and (b) 4 wt.% surfactant and 6 wt.% cosolvent

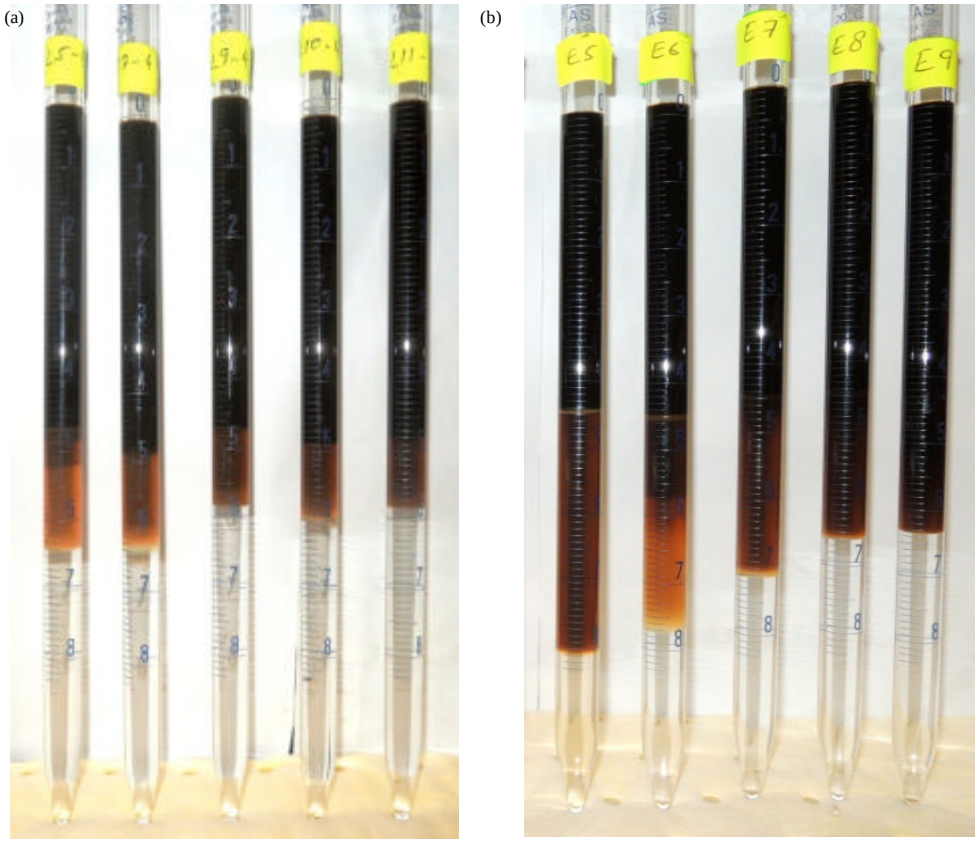

Fig. 2(a-b): Type III microemulsions prepared by (a) 2 wt.% surfactant and 6 wt.% cosolvent and (b) 4 wt.% surfactant and 6 wt.% cosolvent and at 0.2 wt.% salinity increment

salinities were recorded at different time period and plotted verses time. Figure 3 is the plot of microemulsion volume verses time of type III microemulsions prepared with 2 wt.% surfactant and 6 wt.% cosolvent at different salinities. In Fig. 3, it can be seen that microemulsion volume at different salinities is decreasing with time and remains constant after 10 days which is its equilibrium time for this particular formulation (Flaaten *et al*., 2009).

Micromeulsion volumes verses time of 4 wt.% C12-13 AAS and 6 wt.% SBA at three salinities are presented in Fig. 4. It can be noted from Fig. 4 that equilibrium time for this formulation is 20 days. From Fig. 3 and 4, it can be concluded that at same SBA concentration, stabilization time for the formulation having high surfactant concentration is high and vice versa. It can also be seen in both Fig. 3 and 4 that for a particular salinity scan, type III microemulsion at high salinity stabilize sooner as compared to the low salinity type III microemulsion.

Aqueous phase surfactant concentration measurement: The surfactant concentration left in the aqueous phase

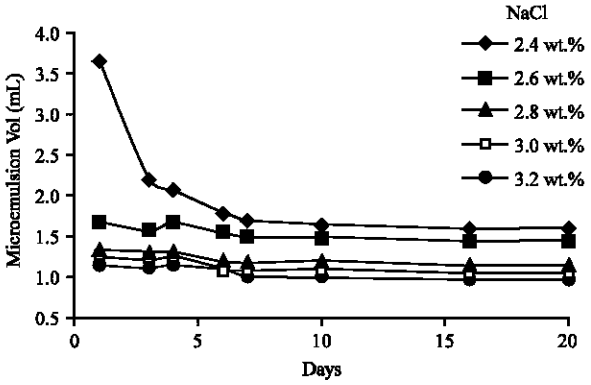

Fig. 3: Type III microemulsion volume vs. time of 2 wt.% surfactant and 6 wt.% cosolvent

was determined by UV visible spectroscopy before and after equilibrium time. By knowing the UV visible spectrum peak of alcohol alkoxy sulfate (208 nm), a straight line calibration curve was generated for various surfactant concentrations as a function of absorbance

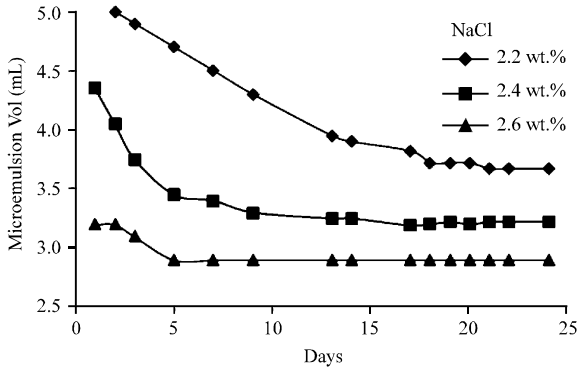

Fig. 4: Type III microemulsion volumes vs time of phase behavior pipettes prepared by 4 wt.% surfactant and 6 wt.% cosolvent

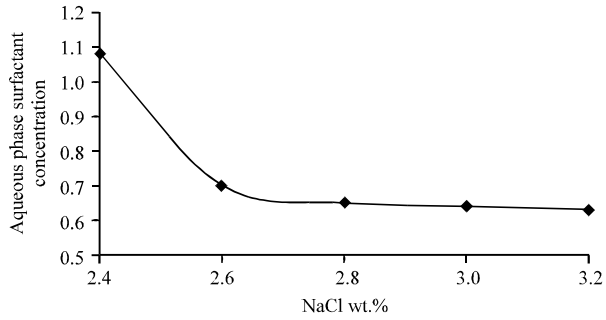

Fig. 5: Aqueous phase surfactant concentration vs. salinity of type III microemulsions prepared by 2 wt.% surfactant and 6 wt.% cosolvent

value. Phase behavior experiments were then performed for various salinities within the type III microemulsion. After achieving equilibrium time, the aqueous phase for each salinity was separated by using syringe connected to long needle for further analysis. The surfactant concentration left in the aqueous phase was then measured by comparing the absorbance value obtained with the initially plotted calibration curve.

Figure 5 shows the surfactant concentration remained in the aqueous phase for various salinities after equilibrium time of 10 days. In this case, the type III microemulsion was generated for various salinities using 2 wt.% surfactant and 6 wt.% cosolvent as shown in Fig. 2a. It can be seen in the Fig. 5 that the increase of NaCl concentration has reduced the amount of surfactant in the aqueous phase. For instance, with 2.4 wt.% NaCl, about 54% of the total surfactant remained in the aqueous phase while only 31.5% was left when the salinity was increased to 3.2 wt.% NaCl. As the salinity increases, surfactants molecules are driven out of aqueous phase and starts contributing more to the middle type III microemulsion phase. This increase of surfactant in the middle phase has increased oil solubilization in microemulsion phase as shown in Fig. 1a.

CONCLUSION

Alcohol alkoxy sulfates has shown good performance in term of oil and water solubilization and its combination with cosolvent has given reduced viscosity clear Type III microemulsion having less equilibrium time.

Distribution of surfactant takes places among aqueous and microemulsion phase of type III microemulsion. For a particular surfactant concentration, the remaining surfactant in the aqueous phase of type III microemulsion is a function of salinity (i.e., surfactant concentration decreases with the increase of salinity). Hence, type III formulation at low salinity is more prone to surfactant loss in which 31% of total surfactant is found in aqueous phase, resulting in unfavorable conditions.

This experimental study has proved that surfactant do not contribute entirely in microemulsion phase. A considerable amount of surfactant remaining behind in the aqueous phase is undesirable due to multiple reasons i.e., adsorption, precipitation and degradation of surfactant and hence reduces the efficiency of surfactant flooding.

REFERENCES

Aoudia, M., W.H. Wade and V. Weerasooriya, 1995. Optimum microemulsions formulated with propoxylated Guerbet alcohol and propoxylated tridecyl alcohol sodium sulfates. J. Dispersion Sci. Technol., 16: 115-135.

Chan, K.S. and D.O. Shah, 1979. The effect of surfactant partitioning on the phase behavior and phase inversion of the middle phase microemulsions. Proceedings of the SPE Oilfield and Geothermal Chemistry Symposium, January 22-24, 1979, Houston, Texas.

Donaldson, E.C., G.V. Chilingarian and T.F. Yen, 1989. Enhanced Oil Recovery, II: Processes and Operations. Elsevier, USA., ISBN: 9780080868738, Pages: 603.

Flaaten, A., Q.P. Nguyen, G.A. Pope and J. Zhang, 2008. A systematic laboratory approach to low-cost, high-performance chemical flooding. Proceedings of the SPE/DOE Symposium on Improved Oil Recovery, April 20-23, 2008, Tulsa, Oklahoma, USA.

Flaaten, A., Q.P. Nguyen, G.A. Pope and J. Zhang, 2009. A systematic laboratory approach to low-cost high-performance chemical flooding. SPE Reservoir Eval. Eng., 12: 713-723.

Flaaten, A.K., Q.P. Nguyen, J. Zhang, H. Mohammadi and G.A. Pope, 2010. Alkaline/surfactant/polymer chemical flooding without the need for soft water. SPE J., 15: 184-196.

Green, D.W. and G.P. Willhite, 1998. Enhanced Oil Recovery. Society of Petroleum Engineers, London, UK., ISBN-13: 9781555630775, Pages: 545.

Healy, R.N., R.L. Reed and D.G. Stenmark, 1976. Multiphase microemulsion systems. Soc. Pet. Eng. J., 16: 147-160.

Hirasaki, G., C.A. Miller and M. Puerto, 2011. Recent advances in surfactant EOR. SPE J., 16: 889-907.

Huh, C., 1979. Interfacial tensions and solubilizing abiiity of a micioeniiilsion pliase that coexists with oil and brine. J. Colloid Interface Sci., 71: 409-426.

Kumar, P. and K.L. Mittal, 1999. Handbook of Microemulsion Science and Technology. CRC Press, New York, USA., ISBN-13: 9780824719791, Pages: 864.

Lake, L.W., 1989. Enhanced Oil Recovery. Prentice Hall, USA., ISBN: 9780132816014, Pages: 550.

Leung, R. and D.O. Shah, 1987. Solubilization and phase equilibria of water-in-oil microemulsions: II. Effects of alcohols, oils and salinity on single-chain surfactant systems. J. Colloid Interface Sci., 120: 330-344.

Levitt, D., A. Jackson, C. Heinson, L.N. Britton, T. Malik, V. Dwarakanath and G.A. Pope, 2006. Identification and evaluation of high-performance EOR surfactants. Proceedings of the SPE/DOE Symposium on Improved Oil Recovery, April 22-26, 2006, Tulsa, Oklahoma, USA.

Nelson, R.C. and G.A. Pope, 1978. Phase relationships in chemical flooding. Soc. Petroleum Eng. J., 18: 325-338.

Pope, G.A., R.S. Schechter, K. Tsaur and B. Wang, 1982. The effect of several polymers on the phase behavior of micellar fluids. Soc. Pet. Eng. J., 22: 816-830.

Sheng, J., 2010. Modern Chemical Enhanced Oil Recovery: Theory and Practice. Gulf Professional Publishing, Houston, Texas, ISBN-13: 9780080961637, Pages: 648.

Winsor, P.A., 1954. Solvent Properties of Am-Phiphilic Compounds. Butterworths Scientific Publication Ltd., London.

Zhao, P., A. Jackson, C. Britton, D.H. Kim, L.N. Britton, D. Levitt and G.A. Pope, 2008. Development of high-performance surfactants for difficult oils. Proceedings of the SPE/DOE Symposium on Improved Oil Recovery, April 20-23, 2008, Tulsa, Oklahoma, USA.