Physicochemical Properties and its Variation Law of Microemulsion Phase When Microemulsion Flooding

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Abstract. The composition change of microemulsion system in microemulsion flooding will inevitably cause the change of phase behavior. Microemulsion with different phase types directly affects its performance and displacement efficiency of microemulsion flooding. Therefore, in order to accurately describe this change, this paper, starting from the composition of microemulsion, gives the physicochemical properties characterization methods of microemulsion phase density, viscosity and interfacial tension, and simulates the change of physicochemical properties of microemulsion phase caused by microemulsion entering the high water-oil ratio zone in the process of flooding. The research results are of great significance for screening microemulsion systems and determining the displacement efficiency.

1 Introduction

Microemulsion is a four-component dispersion system composed of water (or different concentrations of brine), oil, surfactant and cosurfactant. It is usually necessary to make tetrahedron phase diagram to completely reflect the phase change. However, the characterization of such complex phase requires a lot of basic data and tedious experimental data processing. In order to simplify the phase characterization method, the pseudo-ternary phase diagram is generally used [1-5]. That is to say, three pseudo-ternary phase diagram with different component concentrations are intercepted in the tetrahedral phase diagram, and the three pseudo-ternary phase diagram can be connected by the component concentration. In this way, the phase change caused by different component concentrations can be characterized by the pseudo-ternary phase diagram [6-8]. The commonly used pseudo-three phase diagram is generally divided into 2 categories, one is to fix mass ratio of surfactant and cosurfactant, and the other is to fix mass ratio of water and oil. In fact, the mass ratio of water and oil is constantly changing in the process of microemulsion flooding. Therefore, the most commonly used method is the pseudo-three phase diagram method consisting of fixed mass ratio of surfactant and cosurfactant. The phase behavior change of microemulsion can be achieved by changing the concentration and type of surfactant and cosurfactant, the type of oil phase, salinity, water-oil ratio and temperature.

The phase behavior of microemulsion has a direct effect on the performance and displacement efficiency of microemulsion. He Wei and Shen Weiguo [9-10] measured the density of microemulsion system at different temperatures of different water /AOT substances, and studied the variation of apparent mass per unit volume with solute (AOT and water) mass fraction. It is found that the density of microemulsion does not correlate with the concentration of surfactant when the amount of surfactant is below the critical micelle concentration CMC. When the mass fraction of solute is greater than 0.1, the apparent unit mass volume of solute has a linear relationship with its mass fraction. Zhou Bingling and Kong Hui [11-12] selected the twelve-alkyl-sulphate/n-butanol/Na₂CO₃ microemulsion system. It was found that when microemulsion/oil interfacial tension was equal to that of microemulsion/water, the system was the best medium phase microemulsion. The interfacial tension was the lowest, reaching ultra-low interfacial tension of 10⁻³~10⁻⁴mN/m, which had good oil displacement efficiency and residual oil saturation reduced to 16.7%. Therefore, accurately characterizing the changes of physicochemical parameters caused by changes in salinity and water-oil ratio in microemulsion flooding is of great significance for screening microemulsion system and determining displacement efficiency.

2 Physicochemical properties method of microemulsion phase

Surfactant molecules in microemulsion system have two affinity, which can reduce interfacial tension at the oil-water interface, and can also adsorb on the surface of the rock to change wettability. Under the influence of adsorption, the composition of the system changes, which also affects the structure, composition, phase and properties of the microemulsion system. According to
the three phase diagram of microemulsion, the phase state and equilibrium phase composition of any microemulsion system can be accurately determined, and the physicochemical parameters (microemulsion density, viscosity and interfacial tension) of the microemulsion phase are characterized.

2.1 Microemulsion density

The density of water, oil, surfactants and cosurfactant used to prepare microemulsion system at reservoir temperature is determined by ordinary densitometer. Because the salt density cannot be directly obtained, the density of two microemulsions under different salinity can be determined by densitometer, and the parameter $\alpha$ is calculated. Then, according to the composition of the new phase model of different microemulsion systems, formula (1) is used to calculate the microemulsion phase density.

$$\frac{1}{\rho_m} = \frac{C_{1m}}{\rho_1} + \frac{C_{2m}}{\rho_2} + \frac{C_{3m}}{\rho_3} + \frac{C_{4m}}{\rho_4} + \alpha C_{5m}$$  \hspace{1cm} (1)

Where, $k=1,2,3,4,5$—represent water, oil, surfactant, cosurfactant and salinity in microemulsion, $\rho$—component $k$ density, g/cm$^3$; $\alpha$—obtained from laboratory experiments, $C_{km}$—mass fraction of $k$ in microemulsion phase, %.

2.2 Microemulsion viscosity

The viscosity of different microemulsion systems under different salinity was measured by viscometer. According to phase diagram, the viscosity and phase concentration of oil, water and surfactant in different microemulsion systems were calculated, and the viscosity of liquid phase was calculated by formula (2).

$$\mu_m = C_{1m}^{\alpha_1} + C_{2m}^{\alpha_2} + C_{3m}^{\alpha_3} + C_{4m}^{\alpha_4} + C_{5m}^{\alpha_5}$$  \hspace{1cm} (2)

Where, $\alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5$—input parameter.

2.3 Microemulsion interfacial tension

After the microemulsion is injected into the formation, the microemulsion phase is formed, which is different from the water and oil phase. Microemulsion phase produces interfacial tension of microemulsion/oil ($\sigma_{om}$) and microemulsion/water ($\sigma_{ow}$) at the interface between oil and water. At present, the Healy model is often used to calculate the interfacial tension. When the phase composition is determined, the interfacial tension between the microemulsion and the enriched phase ($\sigma_{om}$ or $\sigma_{ow}$) is calculated as a function of the solubility parameter.

W/O type microemulsion/water interfacial tension:

$$\lg \sigma_{om} = \begin{cases} 
\frac{\lg F_\sigma + G_{1m} + \frac{G_{1f}}{G_{1m} C_{1m}}} + \frac{C_{2m}}{C_{3m} > 1.0} \\
\frac{\lg F_\sigma + G_{1f} + G_{1m} + \frac{C_{2m}}{C_{3m}}} + \frac{C_{2m}}{C_{3m}} < 1.0 
\end{cases}$$  \hspace{1cm} (3)

O/W type microemulsion/oil interfacial tension:

$$\lg \sigma_{ow} = \begin{cases} 
\frac{\lg F_\sigma + G_{1m} + \frac{G_{1f}}{G_{1m} C_{1m} + C_{3m} > 1.0} \\
\frac{\lg F_\sigma + G_{1f} + G_{1m} + \frac{C_{2m}}{C_{3m}} < 1.0} 
\end{cases}$$  \hspace{1cm} (4)

Because terms $C_{1m}/C_{3m}$ or $C_{2m}/C_{3m}$ in Healy model are generally greater than 1, and sometimes do not show a linear increasing or decreasing trend in actual calculation. Therefore, the Healy model is improved. The term of $C_{1m}/C_{3m}$ or $C_{2m}/C_{3m}$ in the above formula is modified to $C_{1m}/(1-C_{3m})$ or $C_{2m}/(1-C_{3m})$, and the value range is between 0 and 1.

microemulsion/water interfacial tension:

$$\lg \sigma_{om} = \lg F_\sigma + G_{1f} + \frac{G_{1f}}{G_{1m} C_{1m}/(1-C_{3m}) + 1}$$  \hspace{1cm} (5)

microemulsion/oil interfacial tension:

$$\lg \sigma_{ow} = \frac{\lg F_\sigma + G_{1f} + G_{2f} + \frac{G_{1f}}{G_{2m} C_{2m}/(1-C_{3m}) + 1}}{1-\exp\left[\frac{\sum_{k=1}^{m} C_{km}}{(1-C_{3m})^{2}}\right]}$$  \hspace{1cm} (6)

Where $F_\sigma = \frac{1}{1-\exp\left[\frac{\sum_{k=1}^{m} C_{km}}{(1-C_{3m})^{2}}\right]}$ is calculated. Then, according to the composition of the new phase model of different microemulsion systems, formula (1) is used to calculate the microemulsion phase density.

In the formula, $G_{1f}, G_{1m}, G_{1f}, G_{2f}, G_{2m}$ are all input parameters and can be obtained from experimental data. For W/O microemulsion, $l=\omega$, for O/W microemulsion, $l=\omega$. When there is no surfactant in the system or surfactant concentration is lower than CMC, interfacial tension $IFT=\sigma_{ow}$.

3 Physicochemical properties variation law of microemulsion phase

The variation law of physicochemical properties of microemulsion phase when optimum salinity and salinity changes are studied below.

3.1. When optimum salinity

![Fig. 1. microemulsion phase diagram](https://doi.org/10.1051/e3sconf/202125202066)

At optimum salinity, when water-oil ratio increases, the amount of solubilizing water $C_{1m}(1-C_{3m})$ increases and solubilized oil $C_{2m}(1-C_{3m})$ decreases. The composition
of microemulsion system moves along I right node line to triple point to II left node line, and the microemulsion formation occurs in O/W type microemulsion medium phase microemulsion W/O type microemulsion transformation. On the whole, the microemulsion density showed an upward trend, and the viscosity of the microemulsion increased first and then decreased. Under the optimum salinity, when the mass fraction of water component in oil water is more than 0.2, the viscosity of O/W microemulsion formed by any water mass fraction is lower than that of W/O type microemulsion formed by the same oil mass fraction. The interfacial tension of microemulsion/oil decreases gradually and the interfacial tension of microemulsion/water increases.

3.2 When salinity changes

With the increase of salinity, when the ratio of water to oil increased, the density of O/W microemulsion decreased gradually, the density of W/O microemulsion increased gradually, and the density of microemulsion decreased gradually. The composition of microemulsion system is changed from I, III to II microemulsion, and the viscosity increases first and then decreases. When the salinity is 0.4%, the O/W type microemulsion is formed and the viscosity is 7.98 mPa·s. When the salinity is 1.6%, the viscosity reaches the maximum of 17.46 mPa·s. When the salinity is more than 2.8%, the W/O type microemulsion is formed, the viscosity is 12.04 mPa·s. Compared with the O/W type microemulsion made of similar systems with low salt content, the viscosity of the oil outer phase microemulsion is higher.
Fig. 3. microemulsion physicochemical parameters at different salinity

| Salinity (%) | Type | C_{1m} | C_{2m} | C_{3m} | C_{1m}/(1-C_{3m}) | C_{2m}/(1-C_{3m}) | Viscosity (mPa·s) | interfacial tension \(\sigma_{mo}\) (mN/m) | interfacial tension \(\sigma_{mw}\) (mN/m) |
|--------------|------|--------|--------|--------|-------------------|-------------------|------------------|-------------------|-------------------|
| 0.4 | I | 80.13 | 5.94 | 13.93 | 0.93 | 0.07 | 7.98 | 0.0020 | 0.0268 |
| 0.8 | I | 79.29 | 6.92 | 13.79 | 0.92 | 0.08 | 8.86 | 0.0020 | 0.0222 |
| 1.2 | III (I right) | 71.17 | 16.42 | 12.42 | 0.81 | 0.19 | 14.79 | 0.0021 | 0.0073 |
| 1.6 | III | 60.54 | 27.20 | 12.26 | 0.69 | 0.31 | 17.46 | 0.0023 | 0.0042 |
| 2.0 | III | 43.31 | 43.31 | 13.38 | 0.50 | 0.50 | 17.11 | 0.0028 | 0.0028 |
| 2.4 | III | 24.75 | 64.11 | 11.15 | 0.28 | 0.72 | 13.55 | 0.0046 | 0.0023 |
| 2.8 | III (II left) | 15.19 | 72.24 | 12.56 | 0.17 | 0.83 | 12.04 | 0.0081 | 0.0021 |
| 3.2 | II | 6.92 | 79.29 | 13.79 | 0.08 | 0.92 | 10.76 | 0.0022 | 0.0020 |
| 3.6 | II | 5.94 | 80.13 | 13.93 | 0.07 | 0.93 | 10.61 | 0.0026 | 0.0020 |

Under low salinity, the system is Winsor I type, and the microemulsion/oil interfacial tension \(\sigma_{mo}\) is larger than that of microemulsion/water interfacial tension \(\sigma_{mw}\), increasing the salinity and the microemulsion toward Winsor III transition, microemulsion/oil interfacial tension decreased, solubilizing oil phase ability increased, microemulsion / water interfacial tension increased, water release capacity increased, reached ultra-low interfacial tension (10^{-4}–10^{-2} mN/m), and continued to increase salinity, the system was Winsor II phase state, microemulsion / oil interfacial tension \(\sigma_{mo}\) was smaller than microemulsion/water interfacial tension \(\sigma_{mw}\). When \(\sigma_{mo}\) is equal to \(\sigma_{mw}\), the corresponding salinity is the optimum salinity. This characteristic plays an important role in improving oil recovery by microemulsion flooding.

4 Conclusions
(1) The main influencing factors of phase change are surfactant concentration, additive concentration, salinity, water oil ratio and temperature. By increasing concentration of surfactant and cosurfactant, salinity water-oil ratio and decreasing temperature (ionic surfactant), the system can change from I to III to II.
(2) According to three phase diagram of microemulsion, any microemulsion system containing any total salinity can be obtained, and the main physicochemical parameters such as density, viscosity, and interfacial tension of microemulsion can be established. It can provide basic parameters for numerical simulation of ultra-low permeability reservoir microemulsion flooding.

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References
1. Wang, J. (2008) Theory and application of physicochemical percolation in chemical flooding. Petroleum Industry Press, Beijing.
2. Liu, J. (2009) Phase behavior and solubilization properties of microemulsion formed by amphoteric surfactant DSB. Shandong Normal University, Jinan.
3. Liu, C.W. (2014) Multiphase flow of water in oil emulsion considering hydrate phase transition. China University of Petroleum (East China), Qingdao.
4. Jiang, Q.L., Xin, Y.C., Wang, Y.L. (2000) The phase behavior and stability of oil emulsion by microemulsion flooding. Journal of Jilin Institute of Chemical Technology, (2): 32-36.
5. Pan, J. (2018) Phase behavior and physicochemical properties of green microemulsion system constructed by non-ionic surfactant/long-chain fatty acid ester. Shandong Normal University, Jinan.

6. Suniga, P. T., R. Fortenberry., M. Delshad. (2016) Observations of microemulsion viscosity for surfactant EOR processes. SPE 179669, Tulsa, Oklahoma.

7. Dustin I., W., Christopher, B., Do H.K., et al. (2012) The impact of microemulsion viscosity on oil recovery. SPE154275, Tulsa, Oklahoma.

8. Davidson, A., N. Nizamidin., D. Alexis., et al. (2016) Three phase steady state flow experiments to estimate microemulsion viscosity. SPE179697, Tulsa, Oklahoma.

9. He, W., Shen, W.G. (2010) Density and critical microemulsion concentration of water /AOT/ iso-octane microemulsion system. Journal of Lanzhou University (Natural Science), 46(5):126-128.

10. Webb, E. B., Rensing, P. J., Koh C. A., et al. (2012) High pressure rheometer for in situ formation and characterization of methane hydrates. Energy Fuels, 26: 3504-3509.

11. Zhou, B.L, Kong, H., Zhang, J., et al. (2015) Study on oil displacement effect of medium phase microemulsion. Chemical Engineer, 29(11):35-37.

12. Zhou, B.L. (2016) Preparation of microemulsion and evaluation of its oil displacement effect. Northeast Petroleum University, Daqing.