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Analysis of the effects of alcohol on displacement performance of the micro-emulsion system through ε-β-fish-like phase diagram

D. Yin*, K. Liu, Y. Zhou

College of Petroleum Engineering, Northeast Petroleum University, Heilongjiang, Daqing, 163318

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In the article, a more accurate and intuitive ε-β-fish-like phase diagram is adopted to study the effects of different kinds of alcohols with various concentrations on phase changes of the micro-emulsion system and solubilisation parameters by analyzing the pros and cons of different phase diagrams. We already know that the solubilisation parameters and mid-phase region ranges change with alcohols, so the mixed alcohols composed of n-propanol and n-butyl alcohol (1:1) are chosen as co-surfactants. The micro-emulsion system (1:1 oil-water ratio) is composed of sodium dodecyl sulfonate (AS) with a concentration of 2%, mixed alcohols of 3% and NaCl of 5%. This system is adopted as the formula to conduct the displacement experiments. Compared with the experiments without micro-emulsion or systems with a single type of alcohol, the result shows that this micro-emulsion system can reduce water content by up to 23.7% and increase the displacement efficiency by 13.31% through water displacement. Thus the article has reasonably proved that this formula turns out more effective in terms of water content and displacement efficiency.

Keywords:： Micro-emulsion, ε-β-fish-like phase diagram, Solubilisation parameter, Oil displacement experiment, Alcohol

INTRODUCTION

One of the major advantages of micro-emulsion in the flooding process is the high solubility parameter, ultra low interfacial tension and large middle phase area, which are mainly determined by the properties of surfactant [1-2]. Alcohol, as a type of co-surfactant, can improve the performance of surfactant system [3]. Therefore, it is necessary to understand the effects of different concentrations and types of alcohol on the performance of micro emulsion. In the article, for the study of the range of phase solubilisation parameters of micro-emulsion system, we have chosen the ε-β-fish-like phase diagram method, which can directly estimate the hydrophilic lipophilic degree of surface active agent, three-phase region size and the efficiency of solubilisation of oil and water. We find that the shorter the carbon chain is, the higher the alcohol fraction mass in the interfacial film, or rather, the lower the solubility is, but the larger the middle phase region is [4-5]. As a result, the n-propyl alcohol/n-butyl alcohol is adopted as the assistant surfactant. Then a displacement experiment is carried out by using the AS/mixed-alcohol/octane/NaCl micro-emulsion formulation. The results show that the mixed alcohol system is more effective in terms of water content and displacement efficiency. In the article, an efficient and cost-effective formulation is finally determined by taking only micro-emulsion into account, the results of which could provide a reasonable and reliable basis for future research [6-7-8].

* To whom all correspondence should be sent:
E-mail: yindaiyin@163.com

RESEARCH METHOD FOR THE PHASE BEHAVIOR OF MICRO-EMULSION

The methods to study the phase behavior of micro-emulsion mainly include the Winsor phase diagram, δ-γ-fish-like phase diagram and ε-β-fish-like phase diagram. The Winsor phase diagram can only represent a qualitative phase change state, on the basis of which the δ-γ-fish-like phase diagram and the ε-β-fish-like phase diagram are able to calculate the relevant physicochemical parameters. Besides, parameters obtained from ε-β-fish-like phase diagram tends to be more reliable.

The Winsor phase diagram

The Winsor phase diagram illustrates the phase change in the system, phase volume, the minimum alcohol concentration and alcohol width required for the formation of middle phase micro-emulsion. In the Winsor phase diagram, when the concentration gets low, the system turns into Winsor I micro-emulsion, in which a phase equilibrium is reached between the micro-emulsion and the remaining oil. With the increase of the concentration of alcohol in the system, the middle

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phase micro-emulsion appears and a Winsor III micro-emulsion is formed together with the oil and the water phase. Continue increasing the concentration of alcohol, the middle phase micro-emulsion disappears and the Winsor II micro-emulsion appears with a phase equilibrium of micro-emulsion and residual water. However, when the middle phase micro-emulsion and single phase micro-emulsion are formed, it will be difficult for the Winsor phase diagram to determine the composition of the equilibrium interfacial film and the solubilisation properties of the whole system.

δ-γ-Fish-like phase diagram

The δ in the δ-γ-fish-like phase diagram is a mass fraction between the surfactant and alcohol; γ is the mass fraction of alcohol and surfactant in the system. Therefore, the drawn fish-like phase diagrams seem noticeably "head" up and "tail" down, which describes the whole process of micro-emulsion phase transition. At the point of "fish head", the middle phase micro-emulsion and the "fishtail" single-phase micro-emulsion appears. The area below the “fish belly” indicates the O/W type micro-emulsion and the area above of that means the type of W/O micro-emulsion. The center lines of the “fish head”, ”fish tail” and the “fish belly” in micro emulsion fish-like phase diagram correspond to the equilibrium positions of the lipophilic and hydrophilic action. Therefore, the component of interfacial film can be calculated when the average curvature is zero based on the theory of constant interface composition. δ-γ-fish-like phase diagram has many advantages over the Winsor phase diagram. For example, we can calculate through the fish-like phase diagram the components of the system's composition, the equilibrium interfacial film composition, the surface active agent, alcohol in the oil phase solubility of the middle phase and single phase micro-emulsion. However, the δ-γ-fish-like phase diagram also has its deficiencies. It can not directly reflect the changes of the phase state nor the changes of the volume of each phase. The center line of the three-phase region corresponding to the lipophilic hydrophilic balance equation in this phase diagram appears steeper and it is difficult to obtain an accurate curve, leading to a larger error. Furthermore, E point of “fish tail”, γE, reflects the total mass fraction of alcohol and surfactant in the system, but it fails to reflect directly the least required surface active agent and the amount of alcohol when the single phase micro-emulsion appears.

ε-β-fish-like phase diagram

In the ε-β-fish-like phase diagram, ε is the mass fraction of the alcohols and β is the mass fraction of the surfactants in the micro-emulsion system. Its difference with the δ-γ-fish-like phase diagram is that the “fish head” pitches down and the “fish tail” pitches up, which means the amount of alcohols (ε) that is used to form a mid-phase microemulsion increases as the surfactant content (β) increases. We can see directly from the whole phase diagram that the phase state of the micro-emulsion system changes with the concentration of alcohol. The x-coordinate of the "fish tail" reflects the minimum amount of surfactant required for the formation of single phase micro-emulsion when oil and water are dissolved by the same amount. Y-coordinate reflects the minimum amount of alcohol required. Therefore, we are able to calculate accurately the various physical and chemical parameters through the ε-β-fish-like phase diagram; it can also reflect directly the least surface active agents and the amount of alcohol required for the formation of a single phase micro emulsion and to evaluate the solubilisation ability of the micro-emulsion system more comprehensively. In order to observe the whole process of phase change and to calculate accurately the minimum alcohol concentration required to form the single phase micro-emulsion with the same amount of oil and water, we have compared the solubilisation parameters of different systems according to the characteristics of each phase. In the article, the ε-β-fish-like phase diagram is adopted to study the effects of different concentration and types of alcohol in micro-emulsion system [9-10-11-12].

THE INFLUENCE OF ALCOHOL CONCENTRATION ON PHASE CHANGE OF MICRO-EMULSION

The addition of low carbon alcohol can increase the solubility of the surfactant, and thus increase the ability of the surfactant to tolerate salt, which will finally lead to the phase change state of the system. Therefore, under a certain salinity, a specific alcohol concentration is required for any surfactant to facilitate the formation of a middle phase micro-emulsion system. The ε-β-fish-like phase diagram is adopted to study the phase change state of the system AS/ n-butanol / n-butane /NaCl, and the minimum alcohol content in the formation of the optimum phase micro-emulsion, or the solubilisation property of the system. In the micro-emulsion system, the mass fraction of AS is 2%, the mass fraction of co-surfactant alcohol is

3%, the concentration of NaCl is 5%, the ratio of oil and water is 1:1 [13-14-15-16].

Major instruments and chemicals

Experimental equipment: FA1104 electronic balance, 80-B2 constant temperature box, 800 centrifugal precipitator, Set thermal type DF-101S magnetic heating agitator.

Experimental agents: Twelve sodium alkyl sulfonate (AS) of the analysis grade of purity, used after recrystallization for the experiment, Octane, Butyl alcohol; double deionized water; the other reagents are A.R. grade.

Experimental method

First, add surface active agents with different qualities to a series of test tubes; keep the mass ratio of 5% of brine, and normal octane as 1; drop into different quality alcohol into a series of tubes; place the test tubes in a chamber under a constant temperature of 40 degrees Celsius for a week. When the balance is achieved, take notes of the volume of phase in the test tube.

EXPERIMENTAL RESULTS AND DISCUSSION

Method to determine the position of heads and tails in coordinates

To draw the ε-β-fish-like phase diagram of the AS/ n-butanol / n-butane of /NaCl system, we need first determine the coordinates of heads and tails. The head of coordinates is where the middle phase micro-emulsion begins to appear and the volume is zero. Fish tail coordinate is where water and aliphatic hydrocarbons of the same amount are solubilized completely in single-phase micro-emulsion phase with zero additional volume, that is the moment the middle phase micro-emulsion disappears. When determining the positions of the heads and tails, the reading error is relatively large for the micro-emulsion system subjected to transient changes, thus the extrapolation method is used. First, plot the relations of ratios of the volume fraction of the middle phase micro-emulsion to the entire system (φ) and the mass fraction of the surface active agent to the total volume (β); then fit a straight line. When the value of φ is 0 or 1, the extrapolated values of β corresponds to the abscissas of heads and tails. The relation between φ and β is shown in Fig.1.

According to the linear equation of the relation: $\varphi = 11.11\beta - 0.044$, when φ is 0, $\beta_B = 0.004$ at the fish head; when φ is 1, $\beta_E = 0.094$ at the fish tail.

The ε-β-fish-like phase diagram

The fish-like phase diagram of AS/ butanol / octane /NaCl micro-emulsion system is shown in Fig.2.

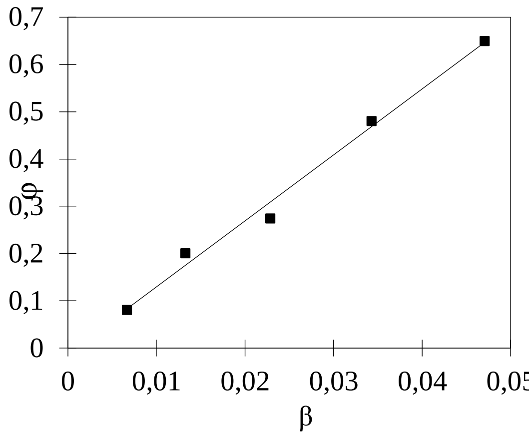

Fig.1. The relation of volume fraction φ-β in middle phase micro-emulsion

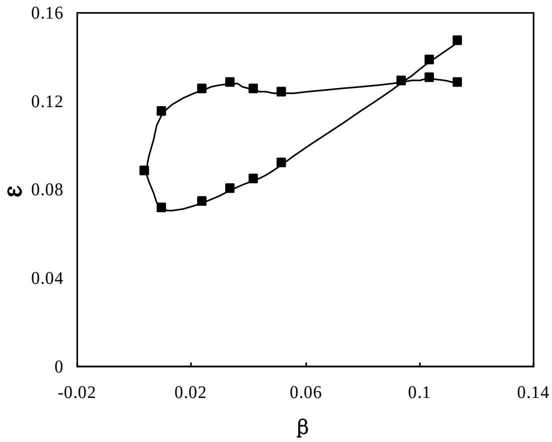

Fig.2. The ε-β-fish-like phase diagram of AS/ butanol / octane /NaCl micro-emulsion system

Concluding discussion

We can see from the fish-like phase diagram that when β remains constant, the whole micro-emulsion system is transformed from type Winsor I to type Winsor III and to type Winsor II with the increase of the concentration of alcohol [5]; with the increase of surface active agent, the alcohol concentration required to form a middle phase micro-emulsion will increase; the alcohol width that corresponds to the ε difference of the middle phase micro-emulsion between appearance and disappearance will decrease. The alcohol width decreases with the increase of surfactant concentration, and is affected by the curvature of the interfacial film, or rather, when surfactant concentration is low, the change of the curvature of the interfacial film from the formation of the middle phase micro-emulsion to its disappearance is larger due to little solubilisation; when the concentration is higher, the change of curvature of the interfacial film gets smaller due to the increasing solubilisation. Therefore, with the increase of surfactant concentration, both the variation amplitude of the curvature of the interfacial film and the alcohol width will decrease.

Statistically, in the system of AS/butanol/ octane/NaCl, when the surfactant concentration reaches 0.004mol/L and the alcohol concentration 0.088mol/L, the middle phase micro-emulsion begins to appear. When the surfactant concentration reaches 0.094mol/L and the alcohol concentration 0.129mol/L, the micro-emulsion disappears, and the single phase micro-emulsion will begin to appear.

THE INFLUENCE OF THE TYPE OF ALCOHOL ON PHASE CHANGE OF MICRO-EMULSION SYSTEM

Alcohol, as a facilitating surfactant, is one of the indispensable factors for the formation of micro-emulsion. Different types of alcohols have different effects on the structure of the interfacial film, and the effect varies due to different types of alcohol to change the optimal salinity of the system by changing the curvature of the micro emulsion droplets either in the form of concave or convex towards the oil phase, so it is necessary to select carefully the best type of low carbon alcohol to increase the solubility of surfactants and thus to improve the efficiency of the surfactant and reduce costs.

Major instruments and chemicals

Experimental equipment: FA1104 electronic balance, 80-B2 constant temperature box, 800 centrifugal precipitator, Set thermal type DF-101S magnetic heating agitator.

Experimental agents: Twelve sodium alkyl sulfonate (AS) of the analysis grade of purity, used after recrystallization for the experiment; Octane, n-propanol, Butyl alcohol, n-amyl alcohol, double de-ionized water; the other reagents are A.R. grade.

Experimental method

First, add surface active agents with different qualities to a series of test tubes; keep the mass ratio of 5% of brine and normal octane as 1; drop different amounts of n-propanol into a series of tubes; place the test tubes in a chamber with a constant temperature of 40 degrees Celsius for a week. After a balance is achieved, take notes of the volume of phase in the test tube. Similarly, the corresponding phase volume data is recorded when the normal butyl alcohol and butyl alcohol are added.

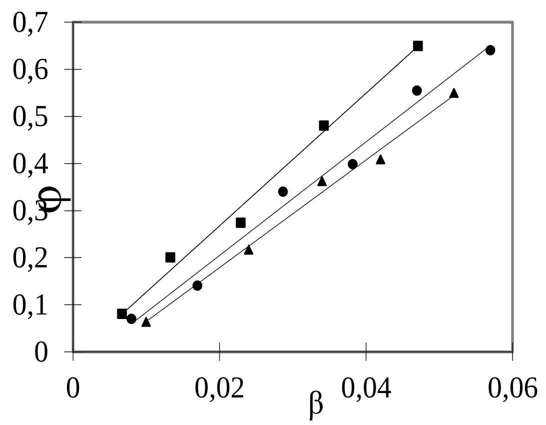

Fig.3. The relation of volume fraction φ-β in middle phase micro-emulsion

Experimental results and discussion

Method to determine the positions of heads and tails in coordinates

The relation between φ and β is shown in Fig.3. According to Fig. 3, when n-propyl is used as co-surfactant in the micro-emulsion system, the fitting linear equation is: $\varphi = 6.58\beta - 0.013$. When φ is 0, $\beta_B = 0.002$ at the fish tail; when φ is 1, $\beta_E = 0.154$ at the fish tail. The fitting linear equation of Butyl alcohol is: $\varphi = 11.11\beta - 0.044$. When φ is 0, $\beta_B = 0.004$ at the fish tail point; when φ is 1, $\beta_E = 0.094$ at the fish tail point. The fitting linear equation of n-amyl alcohol is: $\varphi = 14.085\beta - 0.014$. When φ is 0, $\beta_B = 0.001$ at the fish tail point; when φ is 1, $\beta_E = 0.072$ at the fish tail point.

The ε-β-fish-like phase diagram

According to the calculated results of head and tail coordinates, we have drawn an AS/ n-propyl alcohol (Butyl alcohol, n-pentanol) / octane / NaCl system phase diagram (Fig.4.).

Calculation of physical and chemical parameters of the ε-β-fish-like phase diagram

The dotted line connecting point B and point E is the center line of the three-phase region. The oil-water interface composition of micro-emulsion system in this line has just reached a hydrophilic lipophilic balance. At this moment, the average curvature of the oil-water interfacial film is zero, and the micro-emulsion is the best medium phase micro-emulsion. The HLB equilibrium equation at each point of the center line is:

$$\varepsilon = \frac{A^s - F\alpha}{1 - A^s + F\alpha}\beta + \frac{F\alpha}{1 - A^s + F\alpha} \quad (1)$$

Where

$$F = \frac{A^o S^s - S^o A^s}{1 - S^o - A^o} \quad (2)$$

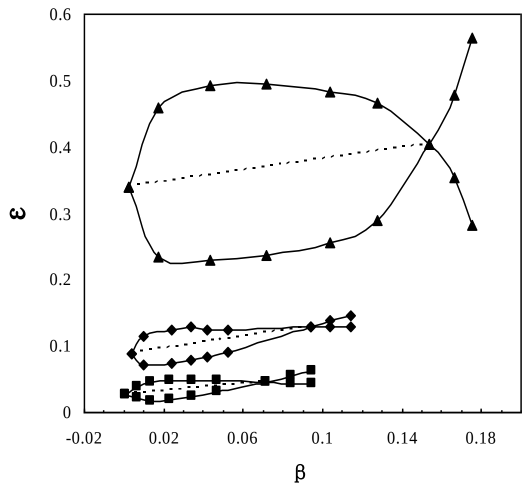

Fig.4. The ε-β-fish-like phase diagram of the AS/ n-propyl alcohol (Butyl alcohol, n-pentanol) / octane / NaCl system

S^O and A^O represent the solubility of the surfactant monomer molecules and the alcohol molecules in the oil phase respectively; S^S and A^S represent the mass fraction of the surfactant and the alcohol in the mixed interfacial film respectively.

The phase center line is a straight line with the slope and intercept as K and I. A^S can be obtained by:

$$A^S = \frac{K + I}{1 + K} \quad (3)$$

S^S can be calculated by:

$$S^S = 1 - A^S \quad (4)$$

Surfactant and alcohol in the interfacial film can be determined by Equation (5,6). When the system has achieved a lipophilic hydrophilic balance:

$$C_S = \beta_E - \frac{\beta_B(1 - \beta_E - \varepsilon_E)}{(1 - \beta_B - \varepsilon_B)} \quad (5)$$

$$C_A = \varepsilon_E - \frac{\varepsilon_B(1 - \beta_E - \varepsilon_E)}{(1 - \beta_B - \varepsilon_B)} \quad (6)$$

Therefore, the mass fraction of the alcohol in the interfacial film can also be expressed as:

$$A^S_{\text{eff}} = \frac{C_A}{C_S + C_A} \quad (7)$$

Surfactant and alcohol solubility in oil phase S^O and A^O can be determined by Equation (8,9).

$$S^O = \frac{\beta_B}{\alpha + (1 - \alpha)(\beta_B + \varepsilon_B)} \quad (8)$$

$$A^O = \frac{\varepsilon_B}{\alpha + (1 - \alpha)(\beta_B + \varepsilon_B)} \quad (9)$$

A^S_{eff} represents the mass fraction of the interface membrane of n-propyl alcohol, Butyl alcohol and n-pentanol alcohol, which are 0.533, 0.372 and 0.232 respectively. The results are consistent with A^S calculated by corresponding systems, which has verified the accuracy of these two methods. All the calculated physical and chemical parameters according to the ε-β-fish-like phase diagram are shown in table 1.

Discussion over the performance of micro-emulsion

We can see from the ε-β-fish-like phase diagram that there are only small differences in the chain length of the three types of alcohols, while the difference in the phase diagram is noticeable. The longer the added alcohol carbon chain is, the smaller the formation of the micro-emulsion phase diagram will be, that is, the smaller the range of the formation microphase emulsion. But A^S decreases from 0.534 to 0.372 then to 0.232, which means that the solubilisation ability of the whole system has become larger, that is: n-pentanol alcohol> Butyl alcohol> n-propyl alcohol.

OIL DISPLACEMENT EXPERIMENT

Through the experiments above, we learn that the chain length of the alcohol is very sensitive to the phase state change of the whole micro emulsion system. In order to obtain a better solubility and a larger middle phase micro-emulsion region, the mixture of n-propyl alcohol / Butyl alcohol will be used as surfactant for oil displacement experiment. The results suggest that the mixed alcohols system has a better displacement efficiency to enhance oil recovery when compared with that of the micro-emulsion system with n-butyl alcohol only.

Table 1. Calculation results of the physical and chemical parameters of the ε-β-fish-like phase diagram.

Alcohol	β_B	ε_B	β_E	ε_E	A^S	S^O	A^O	C_S	C_A	A^S_{eff}
N-propyl alcohol	0.002	0.34	0.154	0.403	0.534	0.003	0.507	0.1526	0.1741	0.533
Butyl alcohol	0.004	0.088	0.094	0.129	0.372	0.007	0.162	0.0906	0.0537	0.372
N-pentanol alcohol	0.001	0.0263	0.0719	0.0453	0.232	0.002	0.048	0.071	0.0214	0.232

Experimental equipment and chemicals

Experimental equipment: core cutting machine, high pressure cleaning apparatus, drying box, vacuum pump, electronic balance, constant speed and pressure displacement pump, piston container, core holder, confining pressure device, thermostat, pressure gauge, cylinder etc.

Experimental agents: twelve sodium alkyl sulfonate (AS) of the analysis grade of purity, used after recrystallization for the experiment; octane; n-propyl alcohol, butyl alcohol, double deionized water, the other reagents are A.R. grade.

Experimental core: 2.5×2.5×30cm Daqing ultra low permeability natural core.

Experimental water: simulated formation water.

Experimental procedure

(1) Connecting device: connect the displacement device, pressure detecting device, liquid collection device and check leakage.

(2) Select full diameter core from Daqing outskirts low permeability oilfield; cut it into a series of cylinder-shaped samples. After extraction, dry them and measure the cores' dry weight, permeability, porosity and size. 3 cores with close permeability and porosity have been selected as experimental cores.

(3) Vacuum the core and saturate them with simulated formation water: immerse the 3 cores selected in simulated formation water; start the vacuum pumping device. Start the time recorder when the pressure of the vacuum gets below 0.098MPa, and vacuum for 24 h. In order to reduce errors, the mass difference of core saturation before and after saturation was measured by the weighing method; then calculate the saturated water volume.

(4) Put the core into the core holder; start flooding until no more oil will be recovered. Record the volume of water in the recovery liquid and calculate the initial oil saturation of the core.

(5) Waterflood the cores and record the outlet oil and water volume at different time and the pressure difference at both ends of the core until the water content of the sample reaches 95%.

(6) Select a piece of core, continue water flooding until the water content reaches 100%. Select another core and start injecting AS/ Butyl alcohol /octane /NaCl micro-emulsion system by 0.5PV and continue water flooding until the water content reaches 100%. Inject the last piece of core with AS/ mixed alcohol /octane /NaCl micro-emulsion system by 0.5 PV and continue water flooding until the water content reaches 100%. Record the oil and water volume in the recovery liquid at different time and the pressure difference at both ends of the 3 cores [17-18-19-20].

Experimental results and discussion

The experimental results without micro-emulsion system, the experimental results with the injection of AS/ Butyl alcohol /octane /NaCl micro-emulsion system and the experimental results with the injection of the AS/mixed alcohol/octane/NaCl micro-emulsion system are showed in table 2.

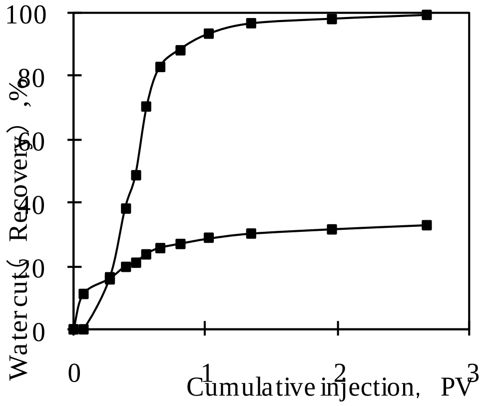

Fig.5. Experimental results of oil displacement without micro-emulsion System

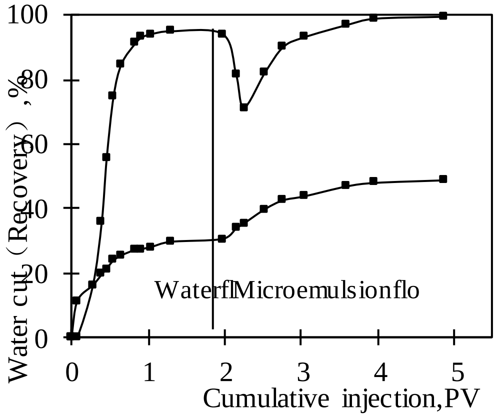

Fig.6. Experimental Results of oil displacement with AS/ Butyl alcohol / octane /NaCl micro-emulsion system.

Table 2. Experimental results.

Core number	Length of core(cm)	Diameter of core(cm)	Porosity(%)	Permeability($10^{-3}\mu m^2$)	Irreducible water saturation(%)	Final recovery(%)
1-1	8.2	2.5	12	7.8	0.34	33.1
1-2	6.7	2.5	15	9.2	0.30	40.60
1-3	7.4	2.5	14	8.4	32	48.7

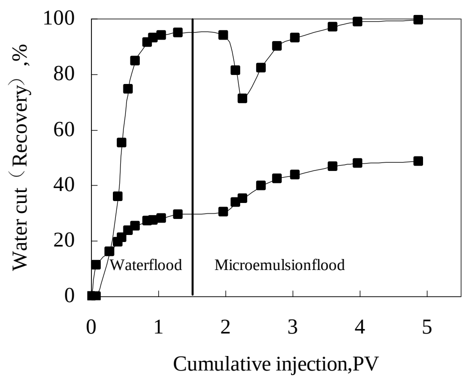

Fig.7. Experimental results of oil displacement with AS/ mixed alcohol / octane /NaCl micro-emulsion system (the proportion of n-pentanol alcohol and butyl alcohol is 1:1)

It can be seen from the results that for low permeability samples, the water flooding recovery is 33.1%. The efficiency reaches 40.6% when Butyl alcohol is used as the co-surfactant in the micro-emulsion system, and 48.7% when the co-surfactant is mixed with alcohol. From the perspective of water ratio, when water ratio reaches around 95%, the micro emulsion can be injected into the water. The water ratio can be reduced by up to 17% for Butyl alcohol and 23.7% for mixed alcohol.

CONCLUSION

In the article, the effects of concentration and the types of alcohol on phase behavior and the solubilisation effects of the AS/ alcohol / octane /NaCl system were studied with the ε-β-fish-like phase diagram. We have learnt that the micro-emulsion system with Butyl alcohol / n-pentanol (1:1) as the co-surfactant has better solubilisation ability and wider middle phase zone. The oil displacement experiment was carried out using the formulation of AS/mixed alcohol/octane/NaCl micro-emulsion system, which is composed of 2% of sodium alkyl sulfonate, 3% of mixed alcohol, 5% of NaCl and an oil and water ratio of 1:1. The results indicate that the system has higher displacement efficiency in practical application.

(1) The ε-β-fish-like phase diagram provides a visual illustration of the phase changes and solubilisation performance of the micro-emulsion system. Meanwhile, the physicochemical parameter such as mass fraction of alcohol in the interfacial film can be calculated more accurately when the system reaches the oil-wet or water-wet balance.

(2) For the AS/ alcohol/ octane /NaCl micro-emulsion system, the alcohol width of n-propyl alcohol is 0.262mol/L, 0.0513mol/L for butyl alcohol, and 0.0291mol/L for n-pentanol alcohol. We can see that in terms of alcohol width, n-propyl alcohol> butyl alcohol> n-pentanol alcohol. From the view of solubility, the minimum alcohol concentration required is 0.403mol/L for the n-propyl alcohol system, 0.129mol/L for the butyl alcohol system, and 0.0453 mol/L for the n-pentanol alcohol system when an optimum medium phase micro-emulsion is to be formed. Thus in terms of solubility properties: n-pentanol alcohol> butyl alcohol> n-propyl alcohol.

(3) AS/ alcohol / octane /NaCl system has a wider range of middle phase micro-emulsion and a better solubility when the mixture of n-propyl alcohol and butyl alcohol (1:1) is used as co-surfactant. We have verified through flooding experiments that the recovery rate of the system with butyl alcohol can be improved by 7.5% than water flooding, meanwhile, the water content can be reduced by up to 17%, while the mixed alcohol system recovery can be improved by 15.6% than water flooding and the water content can be reduced by up to 23.7%.

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