Application of Medium Phase Microemulsion Theory in Enhanced Oil

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Abstract. With the continuous growth of global petroleum resource demand, traditional oil recovery technology is confronted with the challenge of low recovery efficiency in reservoirs characterized by low permeability, low porosity, and high salinity. Therefore, there is an urgent need for more efficient improved oil recovery (EOR) technologies. In the past few years, microemulsion has attracted considerable interest in the petroleum industry as an effective oil displacement agent owing to its remarkable capacity to diminish the interfacial tension that exists between oil and water. Particularly, medium phase microemulsion has emerged as an essential instrument for enhancing oil recovery techniques during extraction processes. This paper systematically discusses the formation mechanism, physical and chemical properties of medium phase microemulsion, as well as its application in EOR. The adaptability and displacement efficiency of microemulsions in complex oil reservoirs are elucidated through analyzing their formation mechanisms such as interfacial adsorption film theory and interfacial tension theory. Additionally, this study explores the impact of environmental variables including temperature, salinity, and pH value on the phase behavior of microemulsions while discussing methods to enhance their stability using nano-composite materials and polymer surfactants. Although challenges exist in field applications such as formula matching and environmental impact associated with medium phase microemulsion technology; however, future integration with intelligent oil displacement technologies offers promising prospects for its development.

Keywords: Medium phase microemulsion, surfactants, microemulsion systems.

1. Introduction

Traditional oil recovery techniques are encountering numerous challenges, particularly in reservoirs characterized by low permeability, low porosity, and high salinity, where recovery rates are significantly diminished. Conventional methods struggle to further enhance oil recovery, resulting in substantial quantities of crude oil remaining trapped within the reservoir. Consequently, the pursuit of innovative technologies to improve oil recovery has become a paramount objective for the oil industry. Microemulsions, as efficient displacement agents, have emerged as a research hotspot in petroleum exploitation owing to their capacity to markedly minimize the interfacial tension that exists between oil and water. These microemulsions exhibit distinctive physicochemical characteristics, notably extremely low tension between the interfaces and high solubility, which demonstrate great potential in Enhanced Oil Recovery (EOR).

The microemulsion in the medium-phase is a transparent, homogeneous three-phase system established within a system comprising oil, water, surfactant, and a low-carbon alcohol. Its core property is the capability to markedly minimize the oil-water interfacial tension to 10^{-3} to 10^{-4} mN/m, thereby enhancing the rate oil recovery. The utilization of medium phase microemulsions within the petroleum sector is primarily focused on conditions of low permeability and complex reservoirs. By enhancing the interaction between the oil and aqueous phases, these microemulsions have the capability to decrease the viscosity of crude oil and improve permeability, thereby improving oil field recovery. Additionally, medium phase microemulsions can inhibit the formation of mineral salts and maintain reservoir permeability, making them a crucial technology in oil exploitation. The application of medium phase microemulsion flooding systems shows significant potential in improving oil recovery, reducing environmental impact, and lowering costs, with broad prospects for future use in complex reservoirs.

2. The Basis of Mid-Phase Microemulsion Theory

2.1. Mechanism of Formation of Medium Phase Microemulsion

During microemulsion development, researchers have proposed four formation mechanisms: the theory of interfacial adsorption film, the theory of interfacial tension, the R ratio theory, and the micelle solubilization theory. These theories explain the process of formation and microemulsions stability from different perspectives.

According to the theory of interfacial adsorption film, the surfactant and cosolvent in the microemulsion form an adsorption film of a certain thickness at the oil-water interface, which can be considered as a tertiary phase. The film interfaces with both the oil phase and the aqueous phase, and the interactions occurring between these two phases influence the bending direction of the film, thus identifying the classification of microemulsion. When the surface tension directed towards the oil phase surpasses that of the water phase, the adsorbed film demonstrates a curvature favoring the oil phase, leading to the creation of a water-in-oil (W/O) microemulsion. Conversely, when the surface tension in the direction of the water phase exceeds that of the oil phase, the film exhibits a curvature towards the water phase to form an oil-in-water (O/W) microemulsion [1].

The interfacial tension theory, suggested by Schulman and Prince, explains that the formation of microemulsions is due to drastic fluctuations in interfacial tension. An elevation in the concentration of active components within the system results in a greater number of molecules interacting and adsorbing at the oil-water interface, which consequently leads to a rapid decline in interfacial tension. When the interfacial tension decreases to a negative value, the interface undergoes spontaneous expansion, which facilitates the accumulation of additional active molecules at the interface. This process ultimately leads to a restoration of the interfacial tension to a positive magnitude. This spontaneous expansion of the interface encourages the formation of the interface facilitates the development of microemulsions while inhibiting the condensation of droplets [2].

The R-ratio theory describes the dual action of surfactants as amphiphilic molecules between the oil phase and the aqueous phase from the perspective of molecular interaction. This interaction influences both the direction of bending and the stability of the interfacial film, which in turn affects the structure and type of microemulsion. The theory describes the interaction

Relationship between surfactants, cosolvents, oil and aqueous phases, as shown in the following formula:

$$R=A_{so}-A_{oo}-A_{ii}/A_{sw}-A_{ww}-A_{hh} \quad (1)$$

Aso and A_{sw} are the cohesive energies associated with surfactants of oil and water interactions respectively, A_{oo} and A_{ww} are the cohesive energies associated with oil and water molecules respectively, A_{ii} is the cohesive energies associated with the hydrophobic regions of surfactant molecules; Ahh is the cohesion energy associated with the head groups of the surfactant.

As R = 1, interface remains rigid and does not exhibit any flexibility; As R < 1, the boundary bends towards the aqueous phase, forming O/W type microemulsion; As R > 1, W/O microemulsion is formed [3]. Micellar solubilization theory holds that microemulsion is formed as a consequence of micellar solubilization. When the concentration of surfactant exceeds its critical micelle concentration, the surfactant molecules will spontaneously aggregate to create micelles, which possess a considerable capacity for solubilization.

2.2. Physical and Chemical Properties of Microemulsion

Microemulsions possess distinct physical and chemical properties that enable their extensive application in fields such as petroleum, medicine, and cosmetics. Firstly, microemulsions have the capacity to markedly decrease the surface tension exist in the interface between oil and water, typically to an ultra-low level of 10^{-2} to 10^{-3} mN/m. This reduction in interfacial tension allows microemulsions to exhibit excellent oil displacement effects, thereby enhancing oil recovery. Additionally, the low viscosity of microemulsions facilitates their flow through porous media. Due to their high interfacial activity, microemulsions can form stable monomolecular films at interfaces, thereby improving their adsorption capacity.

Microemulsions exhibit both dynamic and thermodynamic stability. Dynamic stability refers to the ability of microemulsions to remain stable under external conditions such as stirring, shear forces, or pressure changes. Thermodynamic stability indicates that microemulsions can maintain their phase structure without phase separation over extended storage periods. This stability is ascribed to the limited dimensions of the dispersed phase droplets in microemulsions (generally ranging from 5 to 100 nm) and the effective adsorption characteristics of surfactants at the interface.

Furthermore, the molecular structure and behavior of microemulsions can be comprehensively understood through molecular dynamics simulations, particularly the adsorption and self-assembly behavior of molecules on surfactant at the oil-water interface.

2.3. Classification of Microemulsion Systems

Microemulsions can be classified into three distinct types, which are determined by the variations between the dispersed phase and the continuous phase: oil-in-water (O/W) microemulsions, water-in-oil (W/O) microemulsions, and medium-phase microemulsion systems. In O/W microemulsions, the phase of oil is dispersed within a continuous aqueous phase, making them commonly used in drug delivery and cosmetics. Conversely, W/O microemulsions, where the water phase is dispersed within the oil phase, are frequently utilized in lubricants and coatings.

The formation conditions for bicontinuous microemulsions are unique, typically requiring a specific ratio of oil to water and an appropriate balance of surfactant and cosurfactant. Medium-phase microemulsions differ from the conventional O/W and W/O types. The systems which contains four-phase comprising oil, water, surfactant, and cosurfactant, formed under specific conditions. These microemulsions exhibit unique thermodynamic stability and structural properties, making them effective oil displacement agents in petroleum exploitation. In contrast to conventional microemulsions, medium-phase microemulsions can minimize interfacial tension and maintain stability in environments characterized by elevated salinity and temperature.

The characteristics of the four-phase system are primarily reflected in its complex phase behavior and microstructure. The collaborative interaction between surfactants and cosurfactants plays a vital role in the development of medium-phase microemulsions.

3. Application Mechanism of Medium Phase Microemulsion in Enhancement of Oil Recovery Processes

The mechansim of surfactant and alkaline flooding operates on the principle of producing extremely low interfacial tension. The injection of a polymer in isolation, or the sequential introduction of a surfactant succeeded by the addition of a polymer, can control the flow and thereby enhance oil recovery. Polymers increase the viscosity of water, improving their oil displacement capabilities.

Due to its unique bicontinuous structure, the medium phase microemulsion can more easily navigate the pore network of the reservoir. This structure allows the microemulsion to simultaneously contact both oil and water, enabling it to penetrate areas that are difficult to reach with conventional water or oil flooding. Medium-phase microemulsions promote the separation of crude oil from rock surfaces by diminishing the interfacial tension exists between oil and water. Additionally, their excellent fluidity allows them to efficiently displace remaining oil droplets, thereby improving the efficiency of oil extraction. The distribution of surfactants within the medium-phase microemulsion creates a very thin and flexible oil-water interface, which helps to further reduce interfacial tension. This reduction makes it easier for crude oil to be absorbed from the rock surface, decreasing its tendency to adhere to the pore walls.

Surfactant molecules accumulate at the interfaces between oil and rock, as well as between water and rock, altering the affinity of the rock and making the crude oil easier to mobilize. This shift in wettability is crucial for improving displacement efficiency.

In carbonate reservoirs, microemulsions have been shown to enhance rock wettability and thus increase oil recovery. For instance, studies on the regulation mechanism of nano-microemulsion phase permeability in tight carbonate reservoirs have demonstrated that microemulsions have been demonstrated to significantly decrease the interfacial tension exists between oil and water, which in turn improves the efficiency of oil displacement in sandstone reservoirs. Research has also focused on optimizing microemulsion formulations to enhance their permeability and displacement efficiency in sandstone reservoirs. Due to their unique geological structure, carbonate reservoirs require specific types of microemulsions to regulate wettability. The appropriate microemulsion can improve crude oil recovery in such reservoirs and maintain stability in complex environments. In low permeability reservoirs, the application of microemulsions is more challenging due to the need for better scalability to cover a larger reservoir area. Research in this area often explores how to design microemulsion systems that can operate effectively under low permeability conditions.

4. Design and Optimization of Medium Phase Microemulsion Systems

4.1. Selection of Surfactants and Cosurfactants

Commonly used surfactants can be categorized into four main types: cationic surfactants, anionic surfactants, non-ionic surfactants, and zwitterionic surfactants. In microemulsions, cationic surfactants minimize the tension between oil and water interface, facilitating the formation of microemulsions. Anionic surfactants, characterized by their negative charge, also effectively reduce interfacial tension, contributing to the stability of microemulsions. However, anionic surfactants may react with certain electrolytes, potentially causing instability in the microemulsions. Sodium dodecyl sulfate (SDS), commonly used in higher pH environments, provides excellent detergency and emulsification capabilities. Cetyltrimethyl ammonium bromide (CTAB), a widely used cationic surfactant, is prevalent in antimicrobial and disinfection applications.

The synergistic effect of surfactants and cosurfactants can markedly decrease tension between oil and water interface, promoting the formation of microemulsions. An appropriate combination of surfactant and cosurfactant can prevent the aggregation and flocculation of microemulsions, maintaining their long-term stability. Cosurfactants enhance the fluidity of microemulsions by reducing system viscosity, which is crucial for applications requiring good fluidity, such as drug delivery systems in the pharmaceutical industry.

Primary Alcohol Ethoxylate (AEO) is a mild surfactant frequently used in personal care products like shampoos and body washes. It possesses excellent decontamination ability and biodegradability. AOS has the capability to diminish the tension between water and oil interface, facilitating the dispersion of oil droplets within water, thereby leading to the formation of microemulsions. Ethylene glycol increases the polarity of the system, aiding the surfactant in better dispersing the oil phase, thereby reducing interfacial tension and expanding the microemulsion formation area. When used together, AOS and ethylene glycol effectively reduce interfacial tension, extend the stable area, and improve fluidity and stability.

Alkyl polyglycolide (APG) is a surfactant that does not possess ionic characteristics and is known for its chemical stability and biodegradability. Its utilization in reservoirs characterized by elevated temperatures and high salinity is predominantly associated with enhanced oil recovery (EOR). APG can be used as part of a chemical flooding agent to improve crude oil recovery. By injecting a solution containing APG, the interfacial tension exists between oil and water is diminished, allowing otherwise difficult-to-extract crude oil to flow. In foam displacement technology, APG stabilizes gas foam, increasing its sweeping efficiency in the reservoir.

Zwitterionic surfactants, exemplified by betaine, are integral to the formation of medium phase microemulsions, attributable to their distinctive chemical structure and inherent properties. Characterized by having both positive and negative charges, zwitterionic surfactants establish a compact monolayer at the oil-water interface, leading to a substantial decrease in interfacial tension. This property is essential for the formation of stable microemulsions. Since zwitterionic surfactants remain active across different pH values, they can form stable microemulsions over a wide pH range, enhancing the stability of the microemulsion system.

4.2. Regulation of Microemulsion Phase Behavior

The microemulsions phase behavior is affected by a range of factors like temperature, salinity, and pH value. Changes in these parameters directly impact the development and stability of microemulsions, ultimately affecting their efficacy in enhancing oil recovery. Temperature plays a significant role in regulating the phase behavior of microemulsions. An elevation in temperature alters the molecular configuration of surfactants, leading to the transformation of microemulsions from oil-in-water (O/W) phases to water-in-oil (W/O) phases. Additionally, temperature affects the thermodynamic and kinetic stability of medium phase microemulsions, with higher temperatures potentially causing fluctuations in interfacial tension, thereby influencing the phase state of microemulsions [4].

Salinity, particularly the occurrence of divalent cations like Ca^{2+} and Mg^{2+}, significantly affects the phase behavior of microemulsions. In high-salinity environments, the interaction between cations and surfactant molecules is enhanced, which may lead to the disruption of the interfacial film, shrinking, or even destabilizing the microemulsion phase region. This presents a key challenge for the stability of medium phase microemulsions. To address this, adjusting the ratio of surfactant to cosurfactant can enhance the stability of microemulsions under high-salinity conditions by optimizing their composition [5].

The pH value also influences the charge distribution of surfactant molecules, thereby altering their adsorption behavior and phase state at the oil-water interface. The degree of ionization of surfactants under different pH conditions results in significant changes in phase behavior. Regulating pH can help stabilize the microemulsion system. In oil reservoirs characterized by elevated temperatures and salinity, the synergistic effect of surfactants and cosurfactants is critical. By adjusting their ratio, the phase region of the microemulsion can be effectively extended to adapt to complex reservoir conditions [6].

4.3. Improvement of System Stability

To enhance the stability of microemulsion systems, especially in elevated temperature and salinity reservoir environments, various methods must be employed to prevent phase separation and improve thermal stability. Nanocomposite surfactants are widely regarded as effective tools for enhancing the stability of microemulsions. By introducing nanocomposites such as SiO_2 and TiO_2, it is possible to improve the thermodynamic stability of microemulsions in high-temperature, high-salinity environments and prevent phase separation. These nanomaterials not only increase the mechanical strength of the oil-water interface but also further stabilize the microemulsion system through physical adsorption and chemical bonding [7].

Additionally, polymeric surfactants, such as polyoxyethylene, can significantly inhibit the phase separation of microemulsions. By extending hydrophobic chains or introducing polar functional groups, polymer surfactants can form denser and more elastic interfacial films at the oil-water interface, thereby improving the stability of microemulsions in intricate environments [5]. New modification techniques, such as hydrophobic chain extension and the introduction of functional groups to surfactants, not only improve the thermal stability of microemulsions but also enhance their tolerance under high-salinity conditions [6]. These technical innovations provide crucial support for the practical application of medium-phase microemulsions in oil reservoirs characterized by elevated temperatures and high salinity.

5. Challenges and Prospects of Mid-Phase Microemulsions in Field Applications

Mid-phase microemulsion technology shows great potential in enhanced oil recovery (EOR), but it still faces several challenges in practical applications. One primary issue is the alignment of microemulsion formulation design with reservoir conditions. The geological characteristics, oil quality, and reservoir environments vary significantly across different reservoirs, necessitating tailored adjustments to the microemulsion formulation. Surfactants, cosurfactants, and their proportions must be optimized according to factors such as reservoir temperature, salinity, and crude oil composition to ensure effective oil displacement [8].

The injection process and economic considerations are also critical. Microemulsion injection must be compatible with existing oilfield equipment and processes to prevent clogging or damage. Additionally, the economics of microemulsion injection need comprehensive evaluation, including raw material costs, injection volumes, and the anticipated enhancement in oil extraction efficiency. The current adaptability of microemulsion systems in reservoirs which characterized by elevated temperatures and high salinity levels remains limited, hindering widespread adoption of the technology [9].

From an environmental perspective, the use of microemulsions may pose potential pollution risks, particularly as chemical components can have long-term effects if they enter groundwater layers. Therefore, the environmental impact of microemulsions must be rigorously assessed, and appropriate treatment methods developed, such as optimizing degradation and recycling technologies to mitigate negative environmental impacts. Safety assessments and risk management are equally important. The use of microemulsions involves the transportation, storage, and injection of chemicals, which may carry risks of leakage and contamination. Thus, relevant safety measures and risk control mechanisms need to be strengthened [10].

Intermediate-phase microemulsions can synergize with other improved oil recovery techniques, including polymer flooding and carbon dioxide flooding, to further boost oil recovery. Additionally, the development of smart oil displacement technology presents new opportunities for microemulsion systems. By incorporating intelligent sensors and automated control systems, the injection process of microemulsions can be monitored in real-time, optimizing injection parameters and improving oil displacement efficiency [11]. Furthermore, the integration of nanotechnology and new materials into microemulsion systems has become a research hotspot, promising to enhance adaptability and effectiveness under complex reservoir conditions in the future.

In summary, while challenges related to formulation matching, process design, environmental impact, and safety remain in the field application of medium-phase microemulsions, ongoing technological advancements continue to broaden their prospects in enhanced oil recovery.

6. Conclusion

Medium-phase microemulsion technology demonstrates significant potential in enhancing oil recovery, especially in challenging reservoir environments characterized by elevated temperatures, high salinity, and low permeability. This technology effectively displaces residual oil by markedly minimizing the interfacial tension that exists between oil and water, thereby improving wettability and augmenting the interactions between oil and water. This paper systematically reviews the formation mechanism, physicochemical properties, phase behavior regulation, and application challenges of medium phase microemulsions. The findings indicate that medium phase microemulsions can achieve a stable phase structure and adapt to various reservoir conditions through the judicious formulation of surfactants and cosurfactants.

Despite the challenges in the practical application of medium-phase microemulsion technology in oilfields—such as formulation optimization, injection processes, and environmental safety—these issues are gradually being addressed using new nanocomposite surfactants and modification technologies. In the future, the integration of intelligent oil displacement technology and automated monitoring systems is expected to facilitate the broader application of medium phase microemulsions in oilfield development, further enhancing oil recovery while reducing costs and environmental impact. Consequently, with the continuous development and optimization of this technology, medium phase microemulsion flooding is poised to assume an increasingly significant position within the petroleum sector, providing efficient strategies for improved oil recovery.

Authors Contribution

All the authors contributed equally and their names were listed in alphabetical order.

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