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Brief Introduction to the Research Progress of CO_2 Switchable Surfactant

Haiyan Xiong, Yang Shuai, Haonan Ye, Tianyou Zhang

School of Southwest Petroleum University, Chengdu 637000, China

Abstract

In recent years, switchable surfactants have become the focus of research in this field. Because of their diverse types and wide applications, they have broad prospects for development. This paper discusses the various surfactants are insufficient, expounds the CO_2 switch mode of the development of surface active agent, the structure, mechanism, using the material properties in detail, as well as the typical representative have done according to the research progress of the current existing problems of CO_2 switch surfactant, puts forward the corresponding improvement measures, the future development direction is predicted.

Keywords

CO_2 Switchable Surfactant; Research Progress; Prediction of Trends.

1. Introduction

Surfactants are widespread and indispensable in our life. They are widely used in petroleum industry, cosmetic industry and chemical separation field. Surfactants have a series of physical and chemical functions such as wetting/anti-viscosity, emulsification/demulsification, solubilization, dispersion and washing. However, it is generally difficult to separate from the system, and its practical application will be limited for the system that needs to be separated after its surface active function is completed. If the waste liquid is discharged directly, it will waste resources and pollute the environment. Switchable surfactant can make the molecular structure of surfactant reversible transformation through artificial control, and then realize the reversible and repeated surface activity function, so it can be recycled to solve the above problems.

Currently, the switchable surfactant systems mainly include electrochemical, optical, CO_2/N_2, pH and temperature switchable [1]. Electrochemical switchable surfactants have good effect in laboratory, but their price is high and it is difficult to realize industrialization. The optical switch type only works well in transparent solution or on solid surface; The pH switch type can change the composition of solution. Temperature type surfactant is unstable at low temperature; The oxidation reduction prototype contains ferrocene which is harmful to water quality. CO_2-inducedswitchable surfactants were reported for the first time in 2006, followed by the development of amidine, guanidine, amine and imidazoline systems, but due to the price and synthesis process and other problems, it is difficult to achieve large-scale industrial application, still has a high research value.

By alternately bubbling and removing CO_2 as an environmentally sound trigger, the viscoelasticity of the system can be reversibly "turned on" and "turned off" in several cycles. CO_2 switch type surfactants as environmental stimuli response type intelligent compound, used in the actual environment, with cheap renewable raw materials, recycled, and the advantages of green environmental protection, the emulsion polymerization, emulsification and demulsification, gene transfer, intelligent drug delivery, separation engineering and other fields has great development potential. In this paper, the research progress of CO_2 switchable surfactants in recent years is reviewed.

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2. CO_2 Switchable Surfactant

2.1 Development History of Various CO_2 Switchable Surfactants

As an environmental trigger, CO_2 controls its entry and exit, and the pH value of the system changes accordingly, ionizable groups in the system protonate or deprotonate, and the hydrophilicity and surface activity of the system change correspondingly.

CO_2/ air switchable surfactant can form micelles in water/oil. Such micelle system can effectively demulsify when the switchable surfactant is "inactivated", and become oil-water two-phase. After CO_2 is injected, micelles can be re-formed.

Since 2006, many new systems of CO_2 switchable surfactants have been developed, including amidine[2] guanidine[3] and amine [4]CO_2 switchable surfactants.

2.1.1 Amidine System

CO_2 switchable surfactant, first reported in Science in 2006, is a long carbon chain compound of amidine-based system[5]. After CO_2 is injected into the aqueous solution of this switchable surfactant, the amidine group will be combined with the generated hydrogen ions, and the protonation reaction will make it into hydrophilic bicarbonate or carbonate, so that the conductivity increases rapidly and the viscosity of the system increases. When CO_2 in the solution was discharged, the concentration of H+ in the solution decreased, the amidine group was deprotonated, and the hydrophilic state returned to the hydrophobic state. Studies have shown that cis-trans isomerism of compounds in this process will limit their application in interface chemistry.

The synthesis methods of amidine include direct and indirect methods. The principle of the direct method is to form carbon-nitrogen double bonds through carbonyl aldehyde condensation and addition-elimination reaction. The addition-elimination process is shown in Figure 1:

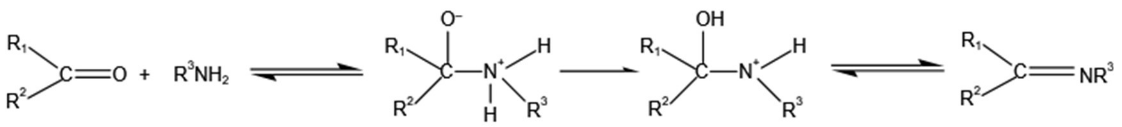

Figure 1. Schematic diagram of addition - elimination process

The action mechanism of amidine-CO_2 switchable surfactant is shown in Figure 2:

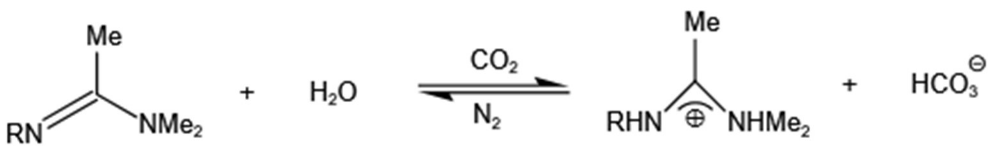

Figure 2. Action mechanism of amidyl CO_2 switchable surfactant

Studies have found that amidine switchable surfactant has strong emulsification and demulsification ability for water/alkane system [6], and the process is reversible, so it can be used repeatedly as both emulsifier and demulsifier.

Zhang Ting et al.[7], under the protection of N2, synthesized N, N' -didodecyl acetamidine with trethyl orthoacetate and dodecylamine as raw materials. Then, in the presence of a small amount of water, CO_2 was injected into its ether solution to generate N, N' -didodecyl acetamidine bicarbonate, which has good surface activity.

2.1.2 Guanidine System

Guanidine-based surfactant has a similar structure and reaction mechanism to guamidine-based surfactant, but the former has a more stable structure and a stronger ability to bind protons, so the

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reaction conditions of its deprotonation reaction process are more demanding, so there are few studies on it at present. The action mechanism of guanidine CO_2 switchable surfactant is shown in Figure 3:

Figure 3. Mechanism of guanidine CO_2 switchable surfactant

Qin Yong [8][9] et al. synthesized dodecyl tetramethyl guanidine CO_2 switchable surfactant (DTMG) and confirmed that dodecyl tetramethyl guanidine could form ionic complex with CO_2 (DTMG·CO_2), and then used as CO_2 switchable surfactant, which could stabilize the solution under normal conditions. After dropping phenolphthalein indicator, red indicated its activity. When heated at 80°C, phenolphthalein solution demulsified and became colorless and inactive.

He Shanshan [10] found that DTMG surfactants had good solubilization ability compared with conventional surfactants and could achieve reversible transformation in the environment.

Chen Shaoyu et al. [11] synthesized and characterized switchable surfactant DTMG with tetramethyl guanidine and 1-Bromododecane as raw materials. DTMG with good foam performance (DTMG·CO_2) is formed through ionization under the action of CO_2, which can be applied in coating foam dyeing system.

2.1.3 Amine System

The amine system includes polyamines, tertiary amines and long chain alkyl groups react to generate CO_2 switchable surfactants. At present, a variety of amine surfactants with CO_2 switchable reaction mechanism have been synthesized, such as inorganic salt resistance, stable emulsion or water-based foam, switchable emulsion and circulating liquid paraffin. The action mechanism of amine CO_2 switchable surfactant is shown in Figure 4:

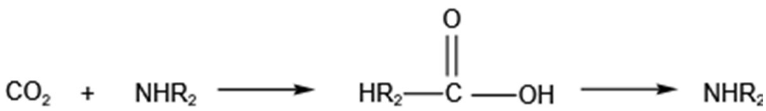

Figure 4. Mechanism of amine CO_2 switchable surfactant

ZHANG et al. [12] synthesized a poly (amine) surfactant, ODPTA, which could change between a low viscosity emulsion and a transparent viscoelastic colloid solution before and after CO_2 was injected and discharged. ZHANG et al. [13] also synthesized a tertiary amine surfactant UC22AMPM, which has been proved to have the same CO_2 switchable reaction mechanism.

Liu Haiyan et al. [14] prepared Gemini CO_2/N_2switchable surfactants with different chain lengths, whose principle is that the linker interacts with N, N-dimethyl alkyl amine, and the surface activity of such surfactants will disappear when CO_2 is discharged.

Cheng Wang et al. [15] synthesized switchable surfactants resistant to inorganic salts by inserting Poly (ethylene glycol) fragments between long-chain alkyl group and tertiary amine group. The mechanism of the surfactant is shown in Figure 5.

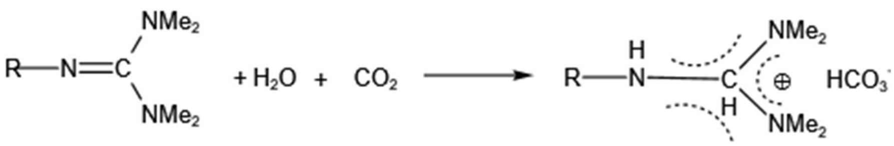

Figure 5. Action mechanism of dodecyl tetramethyl guanidine

Wang Zengzi [16]et al prepared a series of surfactants with switchable ability (D-LCFA) based on the electrostatic interaction between polyether diamine and long-chain fatty acids. Such surfactants have good activity and can stabilize emulsions or water-based foams well. D- LCFA dissociates and recombines during the passage and discharge of CO_2, thereby losing and restoring surface activity, and can be reused.

Tian Li et al. [17] prepared CO_2 switchable polymer P(DEAEMA-SVS) surfactant, and found that it can effectively reduce the surface tension of water, and its aqueous solution can form stable and sensitive CO_2 switchable emulsion with liquid paraffin, and the switchable performance can be cyclic.

Zhang Peng [18] synthesized tetradecyl diethylene triamine. When CO_2 was injected into the solution, the conductivity increased rapidly and pH decreased rapidly, so that the decane/water system formed a stable emulsion. After CO_2 was discharged, pH and conductivity of the solution could be restored to their original state, and the emulsion was demulsified. The results showed that the surfactant had good CO_2 switchable performance.

2.1.4 Other Types

The performance of long chain alkyl imidazoline surfactants switchable from emulsification to demulsification to water chain is not ideal due to the problems of amide emulsification and hydrolysis. If the hydrolysis problem can be overcome, the switchable performance of emulsification to demulsification is good. Its action mechanism is shown in Figure 6.

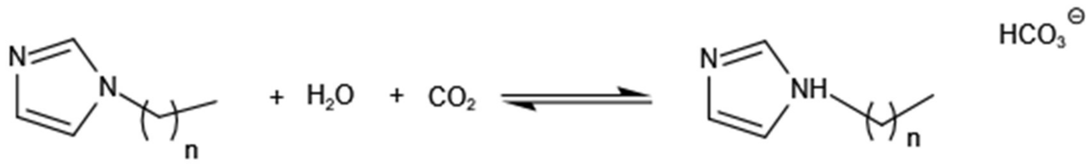

Figure 6. Inactive and reactionable reversible processes of a convertible surfactant

An Chen et al. [19] assembled a new CO_2/ N_2 responsive surfactant by mixing anionic fatty acid (oleic acid) and cationic amine (1, 3-bis (amino propyl) tetramethyl disiloxane) in a 1:1 molecular ratio through electrostatic interaction, which showed good interfacial activity at the oil/water interface and significantly reduced the dosage. Achieve the purpose of cost saving.

2.2 Prediction of Development Trend of Various Types of CO_2 Switchable Surfactants

Wang Gang [20] studied the differences in CO_2/N_2 switchable properties and surface properties between three amidine-based surfactants and one amine based surfactants, and found that the former had better surface appearance, while tertiary amine CO_2/N_2 switchable surfactants had higher reversible efficiency.

The laboratory synthesis of amidine surfactant is expensive and difficult to achieve industrial application. Related to the synthesis of amine CO_2 switchable surfactants, there have been relatively mature synthesis methods, the current synthesis is mainly alkyl tertiary amines, synthesis methods include fatty alcohol method, chlorinated alkylamine method, sodium dodecyl sulfate method. In recent years, more and more researches have been carried out on polyurethane products. However, due to the unclear positioning and structure of functional groups of the products and the lack of mature synthetic routes, it can be regarded as the focus of exploring new products.

3. Summarize and Prospect

CO_2 switchable surfactant [21] has become the focus of the combination of surfactant research and environmental protection work because of its switchable trigger CO_2 gas. CO_2 can be recycled, cheap and easy to obtain, and is the main gas causing the global greenhouse effect. If it can be put into production as a raw material in large quantities, it can not only solve environmental problems, but also make contributions to the chemical industry.

CO_2 switchable surfactant activity can be controlled and most can be repeated use, can to a certain extent, change the rheological properties of system and can be applied to the oil industry, cosmetic industryand chemical separation and so on.

CO_2 switchable surfactants still have many shortcomings. At present, pure CO_2 gas is used in research, which is difficult to obtain directly from the environment. In recent years, more attention has been paid to the related studies of this kind of switched surfactant[22][23][24][25][26].

At present, enhancing the response of surfactant to CO_2 and adjusting its CO_2 response are the focus of research at home and abroad. The former requires the formation of polymers containing multiple amidines [27][28], while the latter introduces amino compounds into the molecular structure of surfactants, such as amino alcohols [29], amino lipids [30], amino acids [31][32].

In short, if a new type of CO_2 gas absorbing material [33] can be developed to directly utilize CO_2 in the air [34] or improve the stability of the existing system [35][36], it can be applied in large-scale industrialization.

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