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Applicability of nonionic surfactant alkyl polyglucoside in preparation of liquid CO_2 emulsion

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ABSTRACT

The essential characteristic of CO_2 makes most surfactants futile to form stable CO_2 emulsion. In this work, a green surfactant named alkyl polyglucoside (APG) was applied to prepare liquid CO_2 emulsion. The performance of surfactant on CO_2 emulsion stability was assessed in a sapphire cell by delamination time of emulsion under the operating conditions about 284.5 K and 5.2 MPa. The results demonstrate that APG has a potential to be used in CO_2 emulsion preparation and the suitable dosage of APG is about 3.0 wt% water quality. The phase-inversion point of water-in-CO_2 and CO_2-in-water was determined as ranging from 15 vol% to 17.5 vol% (water cut) after examining the systems at different water cuts with 3.0 wt% APG. Two surfactants, fatty alcohol polyoxyethylene ether (AEO) and sodium bis(2-ethylhexyl) sulfosuccinate (AOT) were also tested. To consider the applicability of CO_2 emulsion in fields such as submarine hydrate exploitation and CO_2 sequestration, the performance of surfactants in saline solution was examined. The experimental results show that APG can be used as surfactant in preparing liquid CO_2 emulsion with or without NaCl. The adding of 1.0 wt% NaCl for CO_2 emulsion with 3.0 wt% APG was proved to change the phase-inversion point to higher water cut. In comparison, anion surfactant AOT was futile in saline solution.

1. Introduction

It is familiar to us that CO_2 is nontoxic and nonflammable, and one member of atmosphere. It is a kind of chemically inert inorganic substance which derives from a wealth of sources in nature. However, CO_2 is a greenhouse gas which brings more trouble to human. Many scientists paid more attention on CO_2 capture [1,2] and sequestration [3,4] to decrease its greenhouse effect. Moreover, CO_2 will be under supercritical condition when the temperature is above 31.1 °C and the pressure is above 7.38 MPa. There exists many special properties for supercritical CO_2 which had been studied in various fields [5–8].

CO_2 emulsion has been employed in a variety of extraction processes to solubilize hydrophilic substances into CO_2 at first. Subsequently, it has been used in various fields, such as metal nanoparticles [9,10], polymer synthesis [11,12], bioconversion [13], metal-catalyzed [14,15], enzyme-catalyzed [16], and ionic liquid [17]. It is easily recaptured, and recycled use again and generally regarded as a green solvent [18]. For further application of CO_2 emulsion, more fundamental research such as computer simulation [19], phase behavior [20], and emulsion property [21], were performed. However, as a non-polar substance, the intrinsic characteristic of CO_2 often makes it be an exceedingly poor solvent for polar substance such as water and other solutes [22]. This seriously restricts the application of CO_2 emulsion [23,24]. One solution is proposed to add a surfactant with CO_2-philic and hydrophilic groups to make CO_2 emulsion. This has been proven to be a quite successful method and beneficial to broaden the application scope of CO_2 emulsion [25]. To provide a better reagent, the solubility of over 130 commercially available surfactants and related ramifications has been observed in CO_2 at 50 °C and pressures of 100–500 bar by Consan and Smith [26]. Unfortunately, the results confirmed that most conventional surfactants are insoluble in supercritical CO_2 [26]. Even so their finding paved a way to design a CO_2-philic surfactant with commercial viability and environmental responsibility.

In order to solve the problem of most surfactants having low solubility in CO_2, many surfactants were synthesized and tested. Traditional surfactants with alkyl hydrophobic tail were replaced by fluoroether, fluoroalkyl, or silicone groups which could increase the dissolving

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capacity of surfactants in CO_2 and assist polar materials to dissolve in CO_2 [27]. It has been observed that fluorinated compounds are much more soluble in CO_2 than their hydrocarbon counterparts [28]. Most studies have demonstrated that surfactants with dichained [29] or fluorinated alkanes and ethers have favorable interactions to CO_2 [30]. Yazdi et al. [31] has investigated the design and synthesis of highly CO_2 soluble surfactants, dispersants and chelating agents by incorporating the highly CO_2-philic perfluoropolyether tail and a conventional head. Harrison et al. [32] demonstrated that a dichain hybrid surfactant ($C_7F_{15}CH(OSO_3^-Na^+)$ C_7H_{15} or F_7H_7) can form microemulsion. However, the state-of-the-art surfactants used in CO_2 containing fluorine have been proved to be environmentally and commercially unacceptable [33]. In comparison, long twin-tailed anion surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) has been proved to have a good performance on CO_2 microemulsion, except that AOT is extremely insoluble in the presence of CO_2 under these conditions [34].

With regard to traditional surfactants, the hydrophilic/lipophilic balance (HLB) is widely applied in oil-water systems. Analogous to this, the hydrophilic/CO_2-philic balance (HCB) of surfactants is given to the system of CO_2 emulsion. At low HCB values, a surfactant favors CO_2 phase and water-in-CO_2 (W/C) emulsion will form with a low conductivity at proper condition easily. This is because CO_2 has a lower dielectric constant and the continuous phase is CO_2 in W/C emulsions. For high HCB values, a surfactant favors water phase and CO_2–in-water (C/W) emulsions are formed with a high conductivity [35]. In addition, W/C or C/W emulsion formation and stability are related to CO_2 pressure, temperature, salinity, surfactant, water cut and so on [36].

Alkyl polyglucoside (APG) is a green chemical reagent and widely used as surfactant in industry. The objective of this work is to evaluate the performance of APG applied in preparation of CO_2 emulsion. Considering CO_2 emulsion may be applied to exploit natural gas hydrate in future and the water salinity has a great influence on the effect of reagent, NaCl was added to prepare saline solution. The applicability of APG was further studied in different water cut with 1.0 wt% NaCl solution. The suitable dosage of APG was determined from the experimental results and the effect of water cut and salinity were examined for the applicability of APG in W/C or C/W emulsion preparation.

2. Experimental section

2.1. Materials

AOT and NaCl were analytical reagent (AR) grade purchased from Aladdin Industrial (United States). APG and fatty alcohol polyoxyethylene ether (AEO) were the products of Yiqun Chemical Corporation (China). All of the reagents were utilized without further purification. Redistilled water was made in our laboratory. Pure CO_2 (99.9%) was supplied by Beijing Beifen Gases Industry Corporation. An electronic balance with a precision of ± 0.1 mg was used for weighing reagents to prepare aqueous solutions.

2.2. Performance test of CO_2 emulsion

All of the experiments were carried out in a high-pressure transparent sapphire cell to evaluate the behaviors of surfactant on CO_2 emulsion. Fig. 1 illustrates a schematic of the experimental apparatus. The main part of the apparatus is a cylindrical sapphire cell with an effective internal volume of 26 cm^3. It is mounted in an air bath with a view window. This cell is equipped with a magnetic stirrer to accelerate the formation of CO_2 emulsion. The transducers of temperature and pressure are inserted into the cell of which the uncertainties are ± 0.1 K and ± 0.01 MPa, respectively. The temperature fluctuation of air bath is ± 0.1 K. The experimental procedure is as follows:

First, the transparent sapphire cell was soaked and rinsed with redistilled water for about 2 min five times to remove possible residual impurities. After that, high pressure nitrogen was used to blow out extra water. Subsequently, the desired quantity of aqueous solution prepared in advance was charged into the sapphire cell. The vapor space of the cell was then vacuumed to eliminate disturbance of air and the stirrer was turned on to make surfactant disperse in aqueous solution evenly. Meanwhile, the temperature of air bath was adjusted to the desired value. When the temperature in the cell remained constant, the stirrer was turned off and CO_2 was slowly injected into the sapphire cell until the desired pressure was achieved. Thereafter, the stirrer was turned on again at a constant speed in each experiment for 3 h.

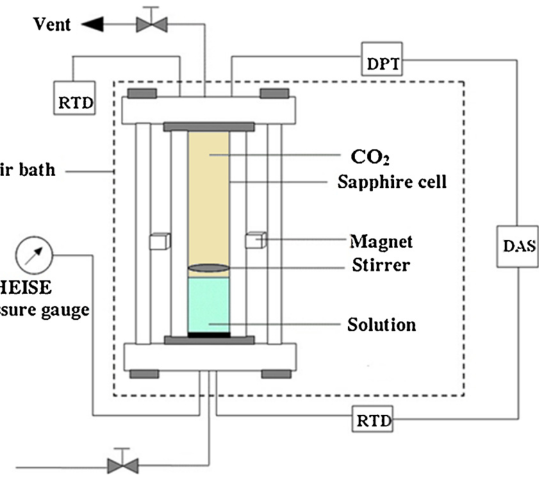

Fig. 1. Schematic of experimental apparatus. DPT: differential pressure transducer; RTD: resistance thermocouple detector. DAS: data acquisition system.

Subsequently, an autoclave with particle video microscope (PVM) and focused beam reflectance measurement (FBRM) probes was applied to evaluate the performance of APG on CO_2 emulsion. The schematic diagram is shown in Fig. 2. The effective internal volume of the autoclave is 535 mL with an operating pressure up to 32 MPa. The temperature of the autoclave was maintained with a thermostat water bath. The magnetic stirrer is installed to mix the fluid to be homogeneous. A temperature transducer and a pressure transducer were mounted in the autoclave to detect the variation of the temperature and pressure with the uncertainties of 0.1 K and 0.02 MPa, respectively. More information on the probes and techniques can be found in our previous papers [37].

The autoclave was first washed with distilled water. Subsequently, the desired quantity of prepared water with APG was charged into the autoclave and then a small amount of CO_2 gas was injected to replace the air three times. The temperature of the water bath was set to the desired value, and the stirrer was started with a constant rotational velocity to disperse the APG in the water phase. When the temperature was stable and maintained constant for about 30 min, CO_2 was injected into the autoclave until the desired pressure was attained and then maintained constant by adding CO_2. The temperature, pressure, PVM pictures, and FBRM chord length distribution of fluid were recorded in real time by the data collection system.

In this work, the performance of an surfactant on CO_2 emulsion is evaluated with the delamination time determined by visual observation in each experimental run. A typical process of emulsification and delamination of CO_2 emulsion in the sapphire cell is shown in Fig. 3. In this group of test, the CO_2 emulsion was prepared with water content of 30 vol% by adding 3.0 wt% APG (based on water content) under 284.5 K and 5.2 MPa. From Fig. 3, one could notice that without stirring, the interface of liquid CO_2 and aqueous solution is clear and distinct during the process of injecting CO_2. At the preliminary stage of stirring, phase interface breaks into smaller drops of liquid quickly. With the elapse of time, the liquid drops become smaller and smaller until the entire system of liquid CO_2 and aqueous solution turn into milky white, which is hardly to observe the drops of water by naked eye. At this time, the emulsion system is not in thermodynamics stable