CO_2-induced smart viscoelastic fluids based on mixtures of sodium erucate and triethylamine

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ABSTRACT

Simple "green" triggers such as CO_2 for switching viscoelastic surfactant solutions between an "on" and "off" state without compromising their inherent properties have been a key focus of research in smart soft matter over the past decade. Here we report a CO_2-induced anionic wormlike micellar fluid by introducing triethylamine (TEA) into natural anionic surfactant sodium erucate (NaOEr) at a molar ratio (C_{NaOEr}:C_{TEA}) of 3:10. When CO_2 is bubbled, pH of the solution decreases from 12.3 to 10.0, and TEA is protonated into a quaternary ammonium salt, which facilitates the growth of micelles as a hydrotrope by screening electrostatic repulsion between the anionic headgroups in NaOEr molecules, resulting in the formation of wormlike micelles and viscoelasticity buildup; upon removal of CO_2, the quaternized TEA is deprotonated back into a non-ionic tertiary amine, thus electrostatic repulsion strengthens and the viscoelastic fluid converting it back to the initial low viscosity spherical micellar solution. Such a reversible sphere-to-worm transition could be repeated several cycles without any loss of response to CO_2 in the pH range of 12.3–10.0, but when further bubbling excess CO_2 to pH < 9.50, the solution transforms into a cloudy dispersion with low viscosity due to the de-neutralization of NaOEr, and this process is irreversible. This study offers a facile way to fabricate smart viscoelastic fluids by incorporating a low-molecular weight CO_2-sensitive hydrotrope with conventional long-chain surfactants.

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1. Introduction

Surfactant-based viscoelastic fluids (VEFs) originating from wormlike micelles (WLMs) have been a key focus of research over the past decade due mainly to their unique micellar structures and rheological response, thus potential applications in various industrial fields [1–3]. Recently, smart viscoelastic fluids (SVEF) [4–12] that respond reversibly to external environmental stimuli and display tunable rheological properties have attracted considerable interest. Up to date, some common stimuli, such as pH [6,7], temperature [7–9], UV/vis [10,11], and redox [12], have been used as triggers to switch the microstructures and thus macroscopic behaviors of VEF. Among which the pH-sensitive VEF is more easily prepared in both laboratory and industrial scales because of its simple designation and fast response. However, the traditional pH-switchable SVEF generally has some disadvantages from the alternate addition of acid/base, for example, the contamination of

the system and the accumulation of the by-product [13–15], deteriorating the viscoelasticity of SVEF. Hence, developing novel stimuli-responsive VEF utilizing simpler and environmentally-benign handle instead of pH is highly desirable.

In the last ten years, CO_2, an alternative of pH, has attracted considerable attentions [14–25] owing to its renewable, cost effective, pollution-free, and energy-efficient characteristics. Although CO_2 essentially acts as pH, it offers additional advantages over the latter as a trigger in avoiding contamination and accumulation in the system, and has been investigated to tune the properties of polymers [16,17], emulsifiers [14], solvents [18], as well as solutes [19], but just a few for switching surfactant-based VEF.

Eastoe et al. [20] pioneered surfactant-thickening of supercritical CO_2 with viscosity enhancement of 20–90% over shear rates 6000–11,000 s^{-1}, which is expected to be used in CO_2 flooding for enhanced oil recovery. Nevertheless, non-supercritical state and immiscibility with oil are always encountered during the CO_2 injection, thus the alternative water-alternating-gas (WAG) [26] displacement is always used. In such a process, CO_2 slug and water slug are alternately injected into the reservoir to increase sweeping efficiency. Because of the heterogeneity of oil reservoirs, the injected CO_2 and water mainly get into highly-permeable

stratum, resulting in a loss of the fluid, and thus decreasing sweep efficiency. If a CO_2-thickening compound is added into water, the viscosity of the slug will increase when it contacts with pre- or post-CO_2 slug, favoring shutting-off large cracks, enlarging sweep area, and then significantly improving oil recovery. When the mixture of CO_2-thickened fluid and oil is produced to the surface together, the viscosity of produced fluid can be quickly decreased by simply depleting CO_2 with N_2 or air, which not only favors the demulsification and the separation of oil/water, but also can recycle the CO_2-switchable VEF.

Based on such an intention, our laboratory recently pioneered the formulation of CO_2-switchable VEF with single octadecyl dipropylene triamine (ODPTA) [21] and *N*-erucamidopropyl-*N*,*N*-dimethylamine (UC22AMPM) [22], respectively. In the absence of CO_2, both ODPTA and UC22AMPM aqueous solutions appear as a low-viscosity emulsion; upon bubbling CO_2 they immediately transform into a transparent viscoelastic gel with ~4,000- or 100,000-fold increase in viscosity; the cloudy low-viscosity fluids can be re-obtained by releasing CO_2. Nevertheless, the surfactants used here are solely obtained through complicated and time-consuming organic synthesis, and the protonated species behave like cationic surfactants which are less biodegradable and more toxic than their anionic counterparts [27–30]. Additionally, the strong adsorption on the solid materials [31] such as the negatively-charged sand surfaces in the oil reservoirs limits the applications of cationic surfactants in oil production.

To address these problems, we designed a simpler and lower-absorption binary CO_2-switchable VEF based on *N*,*N*,*N'*,*N'*-tetramethyl-1,3-propanediamine (TMPDA) and a common commodity anionic surfactant sodium dodecyl sulfate (SDS) at a fixed molar ratio of 1:2 [23]. Bubbling CO_2 protonates TMPDA molecules into quaternary ammonium species, one of which can "bridge" two SDS molecules by non-covalent electrostatic attraction, behaving like a "pseudo" gemini surfactant and forming VEF. Upon the removal of CO_2 by N_2, the quaternized spacers are deprotonated back into tertiary amines, breaking the "pseudo" gemini up back to conventional SDS molecules that form low-viscosity spherical micelles. Jessop and coworkers [24] also demonstrated similar reversible conversion of VEF into spherical micelles when CO_2 is bubbled into or removed out of mixed solution of synthesized sodium octadecyl sulfate and 2-(dimethylamino) ethanol.

Generally, the preparation of VEF by incorporating a CO_2-sensitive hydrotrope into surfactant solutions is simple and cost-effective, but the reported anionic VEF to date displays poor viscosity-enhancement capacity compared to ultra-long-chain VEF [21,22], suggesting that higher surfactant concentration is needed. Therefore, we further improve the VEF by introducing the commercial triethylamine (TEA), a CO_2-switchable hydrotrope [32], into the C22-tailed sodium erucate (NaOEr, Scheme 1) solution with molar ratio of $C_{NaOEr}:C_{TEA} = 3:10$ (referred as "NaOEr–TEA"). Such an ultra-long-chain natural anionic surfactant can decrease surfactant concentration employed, and endow good degradability to the system due to the presence of unsaturated double bond in hydrophobic tail [33].

In this work, we investigated the phase behavior, rheological properties and microstructure of the NaOEr–TEA mixture in the absence or presence of CO_2. With continuously introducing CO_2, this mixture experiences three stages: clear low-viscosity aqueous

solution (pH = 12.30), transparent VEF (pH = 10.00) and cloudy low-viscosity dispersion (pH = 7.35), which have not been found in other worm systems. Note that such a system can be reversibly changed between highly viscoelastic and low-viscosity fluids through several cycles of alternating bubbling and removing CO_2, but it is irreversible when it converts into cloudy dispersions.

2. Experimental section

2.1. Materials

Sodium erucate (NaOEr) was obtained following a previously-reported procedure [7,34] by saponification of natural erucic acid (95%, Sipo Chemical Co. Ltd., China) with an equal mole of NaOH using water/ethanol (v/v: 1:4) as a solvent. The mixture of erucic acid and NaOH was refluxed for 8 h at 80 °C continuously, and then the residual erucic acid and excessive salt were removed by recrystallization twice using cold acetone. Finally, white NaOEr powders were obtained by filtering and freeze-drying.

Triethylamine (TEA, Sigma–Aldrich, $\geqslant$ 99.0%) was used without further purification. Water was triply distilled by a quartz water purification system. All other reagents used in the experiments were of analytical grade.

2.2. Sample preparation

Homogeneous surfactant solutions were obtained by dissolving a designed amount of NaOEr and an appropriate TEA in triply distilled water with gentle agitation at 30 °C, and then left for at least 24 h to reach equilibrium prior to measurements (referred to as "NaOEr–TEA"). All the sample solutions possess the same fixed molar ratio of $C_{NaOEr}:C_{TEA} = 3:10$, unless otherwise stated. The concentration of NaOEr is adapted as that of the solutions.

CO_2 was bubbled into NaOEr–TEA solutions at ambient temperature with a fixed flow rate of 0.1 L min^{-1} for different time under the pressure of 0.1 MPa, and then the pH value of the solutions (referred to as "NaOEr–TEA–CO_2–pH") was determined by a Sartorius basic pH meter PB-10 (±0.01). Next, the corresponding solutions were kept in different sealed vials to avoid contacting with air. To efficiently remove CO_2, N_2 was bubbled into the NaOEr–TEA–CO_2–10 solution with the same flow rate as CO_2 accompanied by heating at 75 °C until the variation of pH levels off. All the samples were kept at 30 °C for about 24 h prior to the following measurements.

2.3. Rheology measurements

Rheological experiments were performed on a Physica MCR 301 (Anton Paar, Austria) rotational rheometer using concentric cylinder geometry CC27 (ISO3219) and stress-controlled mode, with a temperature-controlling Peltier unit and a sample cover to minimize evaporation. Two types of rheological measurements were carried out: oscillatory-shear measurement (frequency sweep tests performed in the linear viscoelastic regime, as determined by dynamic strain sweep measurements) and steady shear-rate scan.

2.4. Cryo-TEM observation

The samples NaOEr–TEA-12, NaOEr–TEA–CO_2-10 and NaOEr–TEA–CO_2-7 were separately embedded on a thin layer of vitreous ice on freshly carbon-coated holey TEM grids by blotting the grids with filter paper, and then plunging them into liquid ethane cooled by liquid nitrogen. Then the vitrified specimen stored in liquid nitrogen was transferred into a JEM2010 cryo-microscope using a Gatan 626 cryo-holder and its workstation. The acceleration volt-
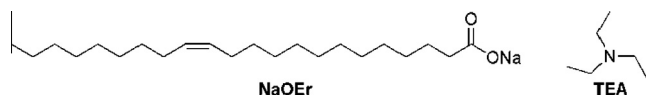
Scheme 1. The molecular structures of sodium erucate (NaOEr) and triethylamine (TEA) used in this work.