Journal of Colloid and Interface Science 470 (2016) 80–91

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Phase behavior and interfacial properties of a switchable ethoxylated amine surfactant at high temperature and effects on CO_2-in-water foams

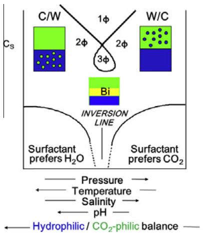
Yunshen Chen [a,1], Amro S. Elhag [a,1], Prathima P. Reddy [a], Hao Chen [b], Leyu Cui [c], Andrew J. Worthen [a], Kun Ma [c,2], Heriberto Quintanilla [a], Jose A. Noguera [a], George J. Hirasaki [c], Quoc P. Nguyen [d], Sibani L. Biswal [c], Keith P. Johnston [a,*]

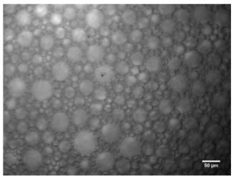
[a] *McKetta Department of Chemical Engineering, The University of Texas at Austin, United States*
[b] *Key Laboratory of Petroleum Engineering of Ministry of Education, China, China University of Petroleum, Beijing, China*
[c] *Department of Chemical and Biomolecular Engineering, Rice University, United States*
[d] *Department of Petroleum and Geosystems Engineering, The University of Texas at Austin, United States*

HIGHLIGHTS

- $C_{12-14}N(EO)_2$ is switchable from a nonionic to a cationic state by lowering pH.
- $C_{12-14}N(EO)_2$ is soluble in brine when cationic and in supercritical CO_2 when nonionic.
- $C_{12-14}N(EO)_2$, effectively lowered the interfacial tension and adsorbed at the C–W interface.
- $C_{12-14}N(EO)_2$ formed viscous C/W foams at harsh conditions (120 °C and 22% TDS).
- C/W foams were shear thinning and consistent with models of foam in porous media.

GRAPHICAL ABSTRACT





ARTICLE INFO

Article history:
Received 7 December 2015
Revised 7 February 2016
Accepted 8 February 2016
Available online 9 February 2016

Keywords:
CO_2-in-water foam
Amine surfactant
Switchable surfactant
High temperature foam
High salinity foam
Phase behavior amine surfactant
Interfacial tension amine surfactant

ABSTRACT

The interfacial properties for surfactants at the supercritical CO_2–water (C–W) interface at temperatures above 80 °C have very rarely been reported given limitations in surfactant solubility and chemical stability. These limitations, along with the weak solvent strength of CO_2, make it challenging to design surfactants that adsorb at the C–W interface, despite the interest in CO_2-in-water (C/W) foams (also referred to as macroemulsions). Herein, we examine the thermodynamic, interfacial and rheological properties of the surfactant $C_{12-14}N(EO)_2$ in systems containing brine and/or supercritical CO_2 at elevated temperatures and pressures. Because the surfactant is switchable from the nonionic state to the protonated cationic state as the pH is lowered over a wide range in temperature, it is readily soluble in brine in the cationic state below pH 5.5, even up to 120 °C, and also in supercritical CO_2 in the nonionic state. As a consequence of the affinity for both phases, the surfactant adsorption at the CO_2–water interface was high, with an area of 207 $Å^2$/molecule. Remarkably, the surfactant lowered the interfacial tension (IFT) down to ~5 mN/m at 120 °C and 3400 psia (23 MPa), despite the low CO_2 density of 0.48 g/ml, indicating sufficient solvation of the surfactant tails. The phase behavior and interfacial properties of the surfactant in the cationic form were favorable for the formation and stabilization of bulk C/W foam at high temperature and high salinity. Additionally, in a 1.2 Darcy glass bead pack at 120 °C, a very high foam apparent

---

[*] Corresponding author at: Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712, United States.
E-mail address: kpj@che.utexas.edu (K.P. Johnston).
[1] Y.C. and A.S.E. contributed equally.
[2] Currently with Total E&P Research and Technology USA LLC.

http://dx.doi.org/10.1016/j.jcis.2016.02.028

viscosity of 146 cP was observed at low interstitial velocities given the low degree of shear thinning. For a calcium carbonate pack, C/W foam was formed upon addition of Ca^{2+} and Mg^{2+} in the feed brine to keep the pH below 4, by the common ion effect, in order to sufficiently protonate the surfactant. The ability to form C/W foams at high temperatures is of interest for a variety of applications in chemical synthesis, separations, materials science, and subsurface energy production.

1. Introduction

The solvent strength of supercritical carbon dioxide (CO_2) ($T_c = 31.1$ °C and $P_c = 1070$ psia) can be appreciable at pressures above the critical pressure (depending upon temperature) where the density is on the order of 0.5 g/ml. However, the van der Waals forces between CO_2 molecules are significantly weaker than for aliphatic hydrocarbon liquids given CO_2's low polarizability [1,2]. Thus, CO_2 solvates hydrocarbon surfactant tails only weakly. Given that the density and solvent strength of supercritical CO_2 are intermediate between those of a gas and a hydrocarbon liquid, dispersions of carbon dioxide and water exhibit characteristics of both macroemulsions (liquid-like CO_2 properties) and foams (gas-like CO_2 properties) [3]. These foams (macroemulsions) composed of water and $scCO_2$ are of interest in numerous fields including reactions and separations in green chemistry [4], materials science, polymer synthesis and separations [5], microelectronics, pharmaceutical particles [6] and subsurface applications including CO_2 sequestration and enhanced oil recovery (EOR) [2,3,7–9].

It is challenging to form water-in-CO_2 (W/C) emulsions with hydrocarbon surfactants given the strong interactions between tails of surfactants adsorbed on the dispersed water droplets, as a consequence of weak solvation by CO_2 [2]. Instead, more expensive fluorinated [10], highly branched [11] or hybrid fluorocarbon/hydrocarbon surfactants [12] are often used to generate W/C emulsions. In contrast, CO_2-in-water (C/W) foams (macroemulsions), are formed readily with numerous hydrocarbon surfactants [3,13]. In this case, the tails are oriented into the CO_2 droplets and thus weak solvation of the tails has a much smaller effect on the interdroplet attractive interactions than in the case of W/C macroemulsions. Therefore, the dispersed CO_2 droplets may be stabilized by a favorable disjoining pressure resulting from electrostatic and steric repulsion between the head groups of the surfactant in the aqueous lamellae [14,15].

Relatively few studies have examined C/W foams at temperatures above ~80 °C [16,17] where the limitations of low surfactant solubility in water or brine and chemical instability become severe [3,18]. For example, nonionic surfactants with ethylene-oxide (EO) head groups are rarely soluble in brine at high temperatures (>100 °C) as the hydrogen bonds between EO and water become weak [19,20]. Whereas ionic head groups can be solvated at elevated temperatures, many anionic surfactants such as sulfates can undergo hydrolysis at high temperature [21] or precipitate in the presence of divalent ions such as sulfonates [22,23]. Furthermore, cationic surfactants such as quaternary ammonium salts often undergo dealkylation by Hoffmann elimination or nucleophilic substitution to form tertiary amines [24]. The lack of soluble and chemically stable surfactants in water and concentrated brine at temperatures above 100 °C has been a major obstacle to the design of high temperature CO_2 emulsions and foams. Such foams are of great interest for raising the viscosity of CO_2 to improve the uniformity of flow (sweep efficiency) in EOR for oil reservoirs where temperatures exceed 80 °C and ionic strengths are ≫1 M, for example, limestone-based reservoirs in the Middle East [25].

The solubility of hydrocarbon surfactants in $scCO_2$ is often limited given its low polarizability/volume and lack of a dipole moment [2,26]. Ionic hydrocarbon surfactants are nearly always insoluble in CO_2 as the weak solvation is not sufficient to overcome the ionic head group interactions [26]. For nonionic hydrocarbon surfactants, the solubility in CO_2 may become substantial upon branching the surfactant tails to weaken the tail–tail van der Waals interactions [27,28], particularly in the case of short EO head groups [2,29]. Furthermore, Chen et al. demonstrated two ethoxylated amine surfactants with linear C_{12-14} tails and 2 or 5 EO groups ($C_{12-14}N(EO)_2$ and $C_{12-14}N(EO)_5$) were soluble at 0.2% w/w in dry CO_2 in the unprotonated state at 120 °C and 3400 psia (23 MPa) [29].

A key property for understanding the interfacial properties of surfactants, in particular, the curvature of emulsions [2,8,30–33] is the CO_2–water (C–W) partition coefficient (surfactant mass fraction in CO_2/surfactant mass fraction in the aqueous phase). The partition coefficient is strongly related to the reciprocal of the hydrophilic/CO_2-philic balance (HCB) (analogous to the hydrophobic/lipophilic balance, HLB, in water and oil systems) whereby

$$\frac{1}{\mathrm{HCB}} = \frac{A_{\mathrm{TC}} - A_{\mathrm{TT}} - A_{\mathrm{CC}}}{A_{\mathrm{HW}} - A_{\mathrm{HH}} - A_{\mathrm{WW}}} \tag{1}$$

where A_{ij} is the interaction potential between CO_2 (C), the hydrocarbon tail (T), water (W) and the surfactant head group (H) [2]. The HCB can be manipulated by altering surfactant structure, temperature, pressure or salinity as depicted in Fig. 1. When 1/HCB < 1, the solvation of the surfactant head group in water is stronger than that of the tail in CO_2, and the surfactant partitions more toward water than CO_2 with the interface curved around CO_2 to form a C/W macroemulsion (or foam) [8]. When 1/HCB > 1, the surfactant partitions more toward CO_2 and the interface curves about water to form a W/C macroemulsion [31–33]. For an HCB very close to unity (balanced state), the interfacial tension (IFT) can become low enough for the formation of a W/C [34,35] or C/W [34] microemulsions. Very near the balanced point, thermal fluctuations create instabilities in the lamellae in C/W macroemulsions that result in coalescence, as described by Adkins et al. [3]. If the HCB is too far above unity, the surfactant adsorption at the interface will be too low to lower the interfacial tension. Thus, the HCB must be chosen in an appropriate window to form stable C/W macroemulsions and foams. When the IFT becomes sufficiently small, ~5 mN/m or less, relatively low shear energy may be utilized to generate a foam by overcoming the capillary pressure to form new interface [19].

To date, the effect of surfactants on the C–W IFT has been studied with nonionic, cationic and anionic/nonionic mixtures at low to moderate temperatures up to 60 °C [27,29,34]. However, above 100 °C, IFTs have been reported for C–W systems without surfactant [36] but rarely for systems containing equilibrated surfactant at the interface [16]. At high temperatures, foams may be expected to be less stable for several reasons. For example, the surfactant solubility in the aqueous phase may become limited. Furthermore, the aqueous lamellae will have a tendency to drain more rapidly as the viscosity of the brine decreases at higher temperatures, unless the surfactant maintains a sufficiently high interfacial viscosity [37]. As the films become too thin, thermal fluctuations in the