Phase Behavior and Interfacial Properties of a Switchable Ethoxylated Amine Surfactant at High Temperature and Effects on CO₂-in-Water Foams

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Abstract

The interfacial properties for surfactants at the supercritical CO₂-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 CO₂, make it challenging to design surfactants that adsorb at the C-W interface, despite the interest in CO₂ – in – water (C/W) foams (also referred to as macroemulsions). Herein, we examine the thermodynamic, interfacial and rheological properties of the surfactant C₁₂₋₁₄N(EO)₂ in systems containing brine and/or supercritical CO₂ 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 CO₂ in the nonionic state. As a consequence of the affinity for both phases, the surfactant adsorption at the CO₂-water interface was high, with an area of 207 Å²/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 CO₂ 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 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 Ca²⁺ and Mg²⁺ 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.

Keywords: CO₂ – in - water foam; Amine surfactant; switchable surfactant; high temperature foam; high salinity foam; phase behavior amine surfactant; interfacial tension amine surfactant.

Introduction

The solvent strength of supercritical carbon dioxide (CO₂) (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 CO₂ molecules are significantly weaker than for aliphatic hydrocarbon liquids given CO₂'s low polarizability.^{1, 2} Thus, CO₂ solvates hydrocarbon surfactant tails only weakly. Given that the density and solvent strength of supercritical CO₂ are intermediate between those of a gas and a hydrocarbon liquid, dispersions of carbon dioxide and water exhibit characteristics of both macroemulsions (liquid-like CO₂ properties) and foams (gas-like CO₂ properties).³ These foams (macroemulsions) composed of water and scCO₂ are of interest in numerous fields including reactions and separations in green chemistry,⁴ materials science, polymer synthesis and separations,⁵ microelectronics, pharmaceutical particles⁶ and subsurface applications including CO₂ sequestration and enhanced oil recovery (EOR).^{2, 3, 7, 8, 9}

It is challenging to form water-in-CO₂ (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 CO₂.² Instead, more expensive fluorinated,¹⁰ highly branched¹¹ or hybrid fluorocarbon/hydrocarbon surfactants¹² are often used to generate W/C emulsions. In contrast, CO₂-in-water (C/W) foams (macroemulsions), are formed readily with numerous hydrocarbon surfactants.^{3, 13} In this case, the tails are oriented into the CO₂ 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 CO₂ 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 temperature²¹ 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 CO₂ emulsions and foams. Such foams are of great interest for raising the viscosity of CO₂ 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 scCO₂ is often limited given its low polarizability/volume and lack of a dipole moment.^{2, 26} Ionic hydrocarbon surfactants are nearly always insoluble in CO₂ as the weak solvation is not sufficient to overcome the ionic head group interactions.²⁶ For nonionic hydrocarbon surfactants, the solubility in CO₂ 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 C₁₂₋₁₄ tails and 2 or 5 EO groups (C₁₂₋₁₄N(EO)₂ and C₁₂₋₁₄N(EO)₅) were soluble at 0.2 % w/w in dry CO₂ 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, 31, 32, 33} is the CO₂-water (C-W) partition coefficient (surfactant mass fraction in CO₂/ surfactant mass fraction in the aqueous phase). The partition coefficient is strongly related to the reciprocal of the hydrophilic/CO₂-philic balance (HCB) (analogous to the hydrophobic/lipophilic balance, HLB, in water and oil systems) whereby

$$\frac{1}{HCB} = \frac{A_{TC} - A_{TT} - A_{CC}}{A_{HW} - A_{HH} - A_{WW}} \quad (1)$$

where A_{ij} is the interaction potential between CO₂ (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 **Figure 1**. When 1/HCB < 1, the solvation of the surfactant head group in water is stronger than that of the tail in CO₂, and the surfactant partitions more towards water than CO₂ with the interface curved around CO₂ to form a C/W macroemulsion (or foam).⁸ When 1/HCB > 1, the surfactant partitions more towards CO₂ and the interface curves about water to form a W/C macroemulsion.^{31, 32, 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/W³⁴ 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 surfactant³⁶ 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 lamellae lead to instabilities that can cause coalescence of the dispersed phase.^{3, 38, 39}

Switchable surfactants exhibit reversibility in various properties including solubility, surface tension and viscosity, which respond to external stimuli including pH, dissolved CO₂ level, light, temperature and magnetic field.⁴⁰ Liu et al. used CO₂ responsive amidine surfactants to stabilize oil/water emulsions.⁴¹ Here, carbonated water switched the inactive nonionic form to an active protonated cationic form that formed emulsions at low temperature and pressure. Zhang et al. reported that the morphology of various classes of surfactants may be switched from spherical micelles to wormlike micelles by dissolving CO₂ gas to lower the pH, resulting in a large increase viscosity of the aqueous phase.^{42, 43}

Recently, a thermally stable⁴⁴ ethoxylated amine surfactant (C₁₂₋₁₄N(EO)₂) was studied at the CO₂ – water interface and shown to stabilize C/W foams with viscosities up to 6 cP at 120 °C in the presence of 182 g/L NaCl brine.^{29, 45} However, this study did not examine the interfacial properties nor the degree of protonation of the surfactant as a function of pH. At low temperature, the degree of protonation of amidine surfactants versus pH has been shown to have a large effect on the thermodynamic and interfacial properties.^{41, 46} Likewise, Feng et al. used a CO₂ - sensitive amine to generate C/W foam at high temperature and pressure without specifying the chemical structure of the surfactant.¹⁷ Given that C/W foams at high temperature are very rare and poorly understood, it would be desirable to develop an understanding of the mechanisms of foam formation and stabilization mechanisms as a function of the thermodynamic, interfacial and rheological properties.

The objective of this study was to demonstrate C/W foams may be formed at high temperatures up to 120 °C, in which the aqueous phase is comprised of concentrated NaCl with or without divalent ions. Here, the foam is stabilized with the surfactant C₁₂₋₁₄N(EO)₂ which was shown to be thermally stable and switchable from the nonionic to the protonated cationic state as the pH is lowered as follows

The degree of protonation was determined versus pH as a function of temperature and salinity, and this behavior was used to explain why the surfactant is soluble in both CO₂ (unprotonated state) and brine (protonated state). The C-W partition coefficient was measured up to 90 °C and 3400 psia along with the effect of surfactant on the IFT at the C-W interface. The phase equilibria and interfacial properties are explained in terms of the interaction of the C₁₂₋₁₄N(EO)₂ head and tail groups with the relevant phases. Furthermore, they are used to provide a thermodynamic basis for understanding of foam formation and

stability at temperatures above 100 °C, which has received very little attention. The foam properties are investigated in a capillary tube and different porous media, which were used to generate the bulk foams. In both the porous media and the downstream capillary, the foam formation, apparent viscosity, and stability mechanisms are described in terms of the surfactant protonation state, phase behavior, and the interfacial properties over a wide temperature range. Remarkably, foams may be generated by injection of the surfactant from either the CO₂ or brine phase, given the solubility of the switchable surfactant in CO₂ in the nonionic state. The rheological behavior of the foams was studied as a function of shear rate in a 1.2 Darcy glass bead pack and described with a simple model for foam in a capillary. Finally, C/W foams were also formed in the presence of crushed calcium carbonate (CaCO₃) given the interest in subsurface applications in limestone reservoirs. Here, excess divalent ions in the brine are shown to depress the dissolution of calcium carbonate, according to the common ion effect, and maintain a low pH required for sufficient surfactant protonation for foam formation.⁴⁷ The ability to measure interfacial properties for stable high temperature surfactants and to understand how they stabilize emulsions and foams is of broad interest in colloid science and for applications including CO₂ sequestration and enhanced oil recovery.

Theory of bulk foam viscosity and stability

A brief theoretical description of the formation, stability, and rheological properties of a bulk foam or emulsion will be presented to provide a perspective for the experimental studies.^{37, 48, 49} Highly concentrated emulsions with an internal phase fraction >0.74 behave as an elastic solid that flows above a yield stress τ_0 and exhibits shear thinning as described by the relationship⁴⁹

$$\mu_{foam} = \frac{\tau_0}{\dot{\gamma}} + 32(\phi_i - 0.73)\mu_e \left(\frac{\mu_e \dot{\gamma} R}{\gamma} \right)^{-1/2} \quad (3)$$

where $\dot{\gamma}$ is the shear rate, γ is the interfacial tension, R is the radius of a spherical droplet, μ_e is the viscosity of external aqueous phase and ϕ_i is internal phase volume fraction (referred to as the foam quality). Further details regarding the formation of bulk foam in terms of a capillary number and the effect of shear thinning on apparent viscosity is given in the supporting information. Bulk foams may be destabilized by drainage of the lamellae film between the dispersed droplets.^{3, 37, 50} The difference in pressure between the thin film section of the lamellae film and plateau border, $\Delta P_{film} = 2(P_c - \Pi_d)$ ⁵⁰ (where P_c is capillary pressure, and Π_d is disjoining pressure) creates a drainage velocity (V)

$$V = -\frac{dh_f}{dt} = \frac{h_f^2}{3\mu_e R_f^2} \Delta P_{film} \quad (4)$$

where R_f and h_f are the radius and thickness for the thin film, respectively. As the lamellae become very thin, thermal fluctuations may rupture the films and produce coalescence.^{3, 38, 39} The probability of hole formation is $\exp(-W_h/kT)$,^{38, 39} where the activation energy (W_h) is given by

$$W_h \cong \frac{h_f^2 \gamma_h^2}{\gamma_p} \quad (5)$$

where γ_p is the interfacial tension of the planar interface and γ_h is the interfacial tension of a curved border of the hole.³⁸

Experimental

Materials

Bis(2-hydroxyethyl) cocoalkylamine ($C_{12-14}N(EO)_2$) (Ethomeen C/12, 97% actives in water) and coco bis(2-hydroxyethyl)methyl ammonium chloride ($C_{12-14}N(EO)_2CH_3Cl$) ammonium salt (Ethoquad C/12, 74-77% actives in 2-propanol) were gifts from Akzo Nobel and used without further purification. Carbon dioxide (Matheson, Coleman grade, 99.99%) was used as received. Sodium chloride (NaCl, certified ACS, Fisher), calcium chloride dehydrate ($CaCl_2 \cdot 2H_2O$, 99+% Acros), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$, Fisher), hydrochloric acid (HCl, technical, Fisher) and isopropanol (certified ACS plus, Fisher) were used as received. Sodium chloride brine was composed of deionized (DI) water (Nanopure II, Barnstead, Dubuque, IA), and NaCl in which the concentration of NaCl from 30 g/L to 182 g/L. In addition, 22% TDS brine (182 g/L NaCl, 77 g/L $CaCl_2 \cdot 2H_2O$, 26 g/L $MgCl_2 \cdot 6H_2O$) was used as model reservoir brine. In some experiments, the initial pH of surfactant water/brine solution/mixture was adjusted from > 8 to any value between 7 and 4 by adding HCl. Calcium carbonate was obtained from Franklin Industrial Minerals. The calcium carbonate was crushed and sieved (20-40 mesh) to obtain diameter size of 420-840 μm . Also, spherical glass beads with diameter of 30-50 μm were obtained from Polysciences, Inc

Cloud-point temperature and potentiometric titration

Cloud-point temperatures were measured up to 120 °C (± 1 °C) with a sealed glass pipette as described in our previous publication.²⁹ The degree of protonation of the surfactant was determined via pH titration with a Mettler Toledo FG2 FiveGo pH meter and a pH/ATC electrode as explained in the supporting information.⁵¹

Interfacial tension measurement between CO₂ and aqueous surfactant solutions

The interfacial tension between CO₂ and aqueous surfactant solutions was determined from axisymmetric drop shape analysis of a captive bubble,⁵² as described in detail previously.³⁴ In the earlier work,³⁴ the maximum temperature was 60 °C. In the current work, the high cloud point of $C_{12-14}N(EO)_2$ enabled IFT measurement over a wide range of temperature from 25 °C to 120 °C. The temperature was raised slowly particularly above 100 °C using two cartridge heaters inserted in the side of the cell. For safety, the entire apparatus was surrounded by 3/8" polycarbonate. The standard deviation of the interfacial tension measurements was typically less than 4 %. The molar surface density of the surfactant monolayer was obtained from the Gibbs adsorption equation below the CMC:

$$\Gamma = -\frac{1}{RT} \left(\frac{\partial \gamma}{\partial \ln C_{surf}} \right)_{T,P} \quad (6)$$

where C_{surf} is the surfactant concentration. The slope was treated as a straight line given the challenges of high temperature measurement. The area occupied by surfactant in the monolayer is given by $A_M = 1/(N_A \Gamma)$ where N_A is Avogadro's number. The efficiency of adsorption was defined as the negative logarithm of the concentration of surfactant in the bulk phase required to produce a 20 mN/m reduction in the interfacial tension: $-\log C_{(-\Delta\gamma=20)} \equiv pC_{20}$.⁵³

Partition coefficient of surfactant between brine and CO₂

To determine the equilibrium surfactant partition coefficient (mass fraction in nonaqueous phase/mass fraction in brine), equal masses (~4 g for each) of CO₂ and brine plus 0.25% w/w surfactant solution, relative to the total weight, were loaded in the front part of a variable volume view cell following our earlier procedure.^{29,34} The temperature of the system was controlled to within ± 0.1 °C by submerging the cell into a water bath equipped with a temperature controller (MP-BASIS, Julabo). After equilibration for two hours, samples of the upper CO₂ phase were extracted via a 6-port valve (Valco Instrument Co., Inc.) and a 50 μ L stainless steel loop (Valco Instrument Co., Inc.). The first 50 μ L were discarded and each sample was obtained by discharging the contents of three loops (150 μ L in total) into a vial with 0.5 mL pH 3 HCl solution. The loop was flushed with a total of 1 mL of pH 3 HCl solution followed with 5 mL of air (1 atm) to recover all of the surfactant and HCl solution. The sampling procedure was repeated three times to collect three separate samples. The concentration of surfactant in each sample was then determined by Epton's method⁵⁴ of two-phase titration with methylene blue solution (colorless endpoint) as described in recent publications.^{29,55,56} The average and standard deviation of the three samples of partition coefficients were reported.

Partition coefficient of surfactant in dodecane over brine and emulsion properties at 25 °C

The partition coefficient and studies of emulsion phase behavior were conducted as a function of pH to help guide the interpretation of the HCB. The partition coefficient of C₁₂₋₁₄N(EO)₂ in dodecane over brine was measured by adding equal volumes (5 mL) of dodecane to 1% (w/w) C₁₂₋₁₄N(EO)₂ in 22%TDS brine solution at different pH values and equilibrating the mixture for 48 hours. The concentration of surfactant in the aqueous phase was determined using methylene blue two phase titration as explained above and in previous publications.⁵⁶ The samples were then mixed using an IKA Ultra-Turrax T-25 with an 8 mm head at 6500 rpm for 2 minutes. Emulsions were formed and the curvature (W/O versus O/W) was determined from the conductivity, measured with a Cole – Parmer EC conductivity meter with Pt/Pt black electrode.

C/W foam formation and apparent viscosity

The apparatus for measurement of the foam apparent viscosity up to 120 °C and 3400 psia is depicted in **Figure 2**. The viscosity of the bulk foam was calculated from the pressure drop across the capillary tube using the Hagen Poiseuille equation. The apparent viscosity (μ) of CO₂ foam in porous media was calculated from the measured pressure drop (ΔP) using Darcy's law

$$\mu = \frac{kA\Delta P}{qL} \quad (7)$$

where k is the permeability of the porous media, q is the volumetric flow rate, L is the length of the sand pack and A is the cross sectional area.

In this work, one of the porous media was a crushed calcium carbonate packed bed (22.9 cm long, 0.62 cm inner diameter tube) with a permeability to water of 76 Darcy (calculated from Darcy's law for 1-D horizontal flow) and 38% porosity (2.6 mL pore volume) determined by the mass of loaded material. For the crushed calcium carbonate (Franklin Industrial Minerals) 420-840 μm in diameter (20-40 mesh), the corresponding pore diameter was 33 – 65 μm as reported by Adkins et al.³ After washing with copious amounts of water and ethanol, the calcium carbonate particles were placed in a tube with a 100 mesh wire screen at each end. A second porous medium was a 1 Darcy (determined by the same method described above) glass bead pack (a 17.9 cm long, 1.73 cm inner diameter tube holding pre-washed 30-50 μm in diameter spherical particles (5 – 8 μm pore diameter) from Polysciences, Inc.). The bed was held in place by 100 mesh and 500 mesh wire screens in series at each end of the tube. The porosity was 36%, and the pore volume is 15.2 mL. The main purpose of the 76 Darcy limestone pack was to rapidly screen surfactants for foaming by using high superficial velocity. The permeability for the 1.2 Darcy pack is closer to that of actual subsurface reservoirs. A 660 μm ID by 1.5 m in length hastelloy capillary tube was used to measure the bulk foam apparent viscosity. Additional details are given in the supporting information. In some cases, the foam effluent from the capillary tube was trapped in a high pressure cell with two sapphire windows inserted in a microscope (Nikon Eclipse ME600) equipped with a Photometrics CoolSNAP CF CCD camera. The micrographs were analyzed using ImageJ for the bubble size and distribution, as described previously.³

PHREEQC simulation

The composition of brines and pH at equilibria were calculated with an excess high pressure CO₂ phase in the presence/absence of calcium carbonate in terms of the phase behavior and chemical equilibria with PHREEQC (Version 2.18). The calculation included the dissociation of CaCO₃, MgCO₃ and CaMg(CO₃)₂, acid-base reactions of divalent ions, and carbonic acid-bicarbonate-carbonate equilibria) along with phase equilibria of CO₂ between the gas and liquid phases. Additional details are given in the supporting information.

Results and Discussion

The results and discussion are presented in four main sections. The first three describe phase behavior in aqueous media, phase behavior in CO₂, and interfacial properties. The results in these three sections are used as a basis to understand the last section on the properties of bulk foam and foam in porous media.

Bulk phase behavior of the surfactant: cloud point temperatures and degree of protonation

The phase behavior of the surfactant and the degree of protonation were studied in brine versus pH, salinity and temperature (in these experiments CO₂ was not present). The cloud point temperatures for a 1% w/w C₁₂₋₁₄N(EO)₂ aqueous solution with pH values between 4 to 7 and salinities between 0 to 22% TDS are listed in **Table 1**. They increased with a decrease of pH for all salinities tested. At lower pH the surfactant will be shown to be cationic and solvated more effectively by the brine. At a pH less than or equal to 5.5, the cloud points of the surfactant are higher than 120 °C, while at pH 7, the surfactant was not completely soluble, irrespective of salinity.

Effect of temperature. The degree of protonation versus pH was calculated from pH titration curves as a function of temperature and salinity (**Figure 3**). For each curve, the surfactant is fully soluble at low pH in the protonated state. As the pH is increased, the surfactant solution becomes turbid indicating phase separation of the surfactant at a value depicted by the red circle. The degree of protonation versus pH for 1% w/w C₁₂₋₁₄N(EO)₂ in 22% TDS brine at 24, 50 and 90 °C is shown in **Figure 3A**. At a pH below 5.4, the surfactant was fully protonated at each temperature. At higher pH values, the degree of protonation decreased with an increase in temperature at a given pH, as indicated by a downward shift of the curves. For example, at pH 6.2, 98% of the surfactant was protonated at 24 °C, compared to only 65% at 90 °C. Exothermic protonation has been reported for alkyl and hydroxyalkyl substituted amines at lower temperatures.^{51, 57, 58, 59} The heat released may be attributed to the binding of the solvated surfactant amine head group with the hydronium ion, and formation of hydrogen bonds of structured water at the surface of the tails.^{58, 60}

Effect of salinity at 90 °C. The degree of protonation versus pH for 1% w/w C₁₂₋₁₄N(EO)₂ at 90 °C in water, 120 g/L NaCl brine and 22% TDS brine is shown in **Figure 3B**. At a given pH, it increases with salinity as shown by the upward shift of the curves. For example, at pH 5.3, the degree of protonation of the surfactant was 71% in water and 100% in 22% TDS brine. At surfactant concentration of 1% w/w, the majority of C₁₂₋₁₄N(EO)₂ surfactant will be shown below in the interfacial tension section to be in the micellar state. The protonation of the amine head groups will be inhibited by the electrostatic repulsion between the resulting cations at the palisade micelle surface and the free hydronium ions in the bulk solution. This charging becomes more favorable with an increase in the Cl⁻ concentration as the double layer screens this electrostatic repulsion between the surfactant cations and hydronium ions. Thus,

protonation of the surfactant is favored with an increase in salinity as observed. A similar mechanism has been provided to describe the effect of salinity on micelles composed of anionic surfactants.⁶¹

Effect of pH. The effect of pH on the cloud point temperature of $C_{12-14}N(EO)_2$ depends upon the solvation of surfactant headgroup and tail. At a pH equal to or below 5.5, the surfactant is highly protonated (above 97% for 24 to 90 °C as shown in **Figure 3A**). The protonated amine is more strongly solvated with an increase of temperature, because of greater dissociation of protonated amine and counterions with higher thermal energy.⁶² Furthermore, the solvation of the hydroxyethyl groups decreases with an increase of temperature, due to weakening of hydrogen bonding.^{3, 19} Finally, the solvation of the hydrocarbon tail in water increases with temperature, as the structure of water about the hydrophobic tails is more disordered at higher temperatures.^{60, 52, 55} At low pH, the high solubility suggests that, the increase in solvation for both protonated nitrogen atom and hydrocarbon tail with temperature exceeds the reduction in solvation of EO group. At a pH above 7, only about 27% of the surfactant is protonated at 90 °C in 22% TDS brine. Here, the small amount of protonated $C_{12-14}N(EO)_2$ does not provide sufficient electrostatic repulsion between micelles to solubilize $C_{12-14}N(EO)_2$ at any temperature (**Table 1**).

Effect of pH on oil/brine partition coefficient and type of emulsion. In order to further understand the nature of the switchable surfactant, the oil/brine partition coefficient and the emulsion curvature (either W/O or O/W) was determined as a function of pH. The oil/water (O-W) partition coefficient of 1% (w/w) of $C_{12-14}N(EO)_2$ between 22%TDS brine and dodecane at 25 °C as a function of pH is shown in **Figure 4**. The O-W partition coefficient is below 0.1 for a pH below 4 and increases gradually to 3 at pH of 8.2. As the degree of protonation decreases with increasing pH (**Figure 3**), the hydrophobic nonionic (unprotonated) state is more favored causing migration of surfactant to the oil phase. As expected, the emulsion inverts from O/W to W/O when pH is increased from 7.5 (conductivity= 50.3 mS/cm) to 8.2 (conductivity = 8×10^{-4} mS/cm) with the increase in partition coefficient as shown in the photos in **Figure 4**. The change from O/W to W/O is consistent with Bancroft rule where the surfactant prefers the continuous phase, for example oil for a partition coefficient >1 above pH 7.5. Similarly, Golec et al. found for $C_8N(EO)_2$ an increase in the pH from 6.5 to 10.5 increased the oil/water partition coefficient from 0.026 to 6.84.⁵⁷ Finally, Mercado et al. showed the evolution of emulsion type from O/W to W/O by increasing the pH for alkylamine surfactants.⁶³

Solubility in CO₂ and CO₂-brine partition coefficients of $C_{12-14}N(EO)_2$

Because of the equilibrium between the nonionic and protonated cationic forms (**Equation 2**) for the switchable surfactant, it will now be shown to be soluble in CO₂ as well as brine. The solubility in

CO₂ and CO₂-brine partition coefficient are important properties for understanding the subsequent sections on interfacial properties and foam behavior.

Solubility in CO₂. The surfactant, C₁₂₋₁₄N(EO)₂ was reported recently to be soluble in CO₂ at 0.2% w/w up to 120 °C.²⁹ As the temperature increases, the cloud point pressure for dissolution of the surfactant increases, in order to maintain a sufficient CO₂ density. In dry CO₂, C₁₂₋₁₄N(EO)₂ is unprotonated and thus nonionic, which favors CO₂ solvation. Also, the presence of only two hydroxyethyl groups results in weaker intramolecular hydrogen-bonding,²⁸ which favors solvation, relative to the case of alkyl EO/PO surfactants with larger numbers of EO groups.²⁸ Furthermore, the decrease of cloud point density with increasing temperature indicates that thermal energy overcomes surfactant tail-tail interaction and weakens intramolecular hydrogen-bonding, and thus improves the solvation.^{28, 29} For ionic hydrocarbon surfactants, the weak solvation by CO₂ as a consequence of its low polarizability/volume, is usually insufficient to overcome the lattice energy of the ionic head group.²⁶

CO₂/brine partition coefficient. The partition coefficients of 0.25 % w/w C₁₂₋₁₄N(EO)₂ between CO₂ and 182 g/L NaCl or 22% TDS brine at 24-90 °C and 1000 or 3400 psia are listed in **Table 2**. At 3400 psia, a low C/W partition coefficient (~0.03) was found at all temperatures and salinities with CO₂ densities between 0.61 to 0.94 g/ml. In the presence of high pressure CO₂, the pH of CO₂ saturated aqueous phase is ~3.⁶⁴ Here, C₁₂₋₁₄N(EO)₂ is highly protonated as demonstrated in **Figure 3**. The cationic headgroup is solvated by ion-dipole interactions (high A_{HW}).⁶⁵ The solvation of the straight chain hydrocarbon tail in CO₂ is relatively weak due to the weak van der Waals attraction between CO₂ and the surfactant tail (low A_{TC}). The much smaller numerator in **Equation 1** relative to the denominator (high HCB) leads to a low C/W partition coefficient. This HCB value will be shown to favor curving of the C-W interface about CO₂ for formation of a C/W macroemulsion.⁸ In addition, there is an interesting compensation of the solvation of the various parts of the surfactant molecule at 3400 psia as the temperature increases. The solvation in brine of the protonated nitrogen increases, while that of the hydroxyethyl groups decreases. The increase in thermal energy increases tail solvation in CO₂ by overcoming tail-tail interactions, but the lower density of CO₂ also leads to a reduction in the solvent strength of CO₂.² These compensating changes appear to cancel each other out such that the partition coefficient is approximately constant.

The C/W partition coefficient decreased with a decrease of pressure at constant temperature as expected. At 90 °C, it decreased from 0.028 at 3400 psia to below 0.004 (detection limit) at 1000 psia. This pressure reduction should not significantly affect solvation of either the protonated nitrogen atom or hydroxyethyl groups in the aqueous phase. However, at these conditions, the decrease in CO₂ density (and thus solvent strength) from 0.61 to 0.12 g/mL causes a significant decrease of C-W partition coefficient

for $C_{12-14}N(EO)_2$. Furthermore, it has been demonstrated that $C_{12-14}N(EO)_2$ is not completely soluble at 0.2% w/w in dry CO_2 at 1000 psia and 90 °C.²⁹

Interfacial properties at CO_2 -22% TDS brine interface up to 120 °C

Because the surfactant has been shown to be soluble in both brine and CO_2 , it may be solvated by each phase when adsorbed at the CO_2 -water interface. The experiments in this section were performed at pH 3, given the formation of carbonic acid from the high pressure CO_2 , where the surfactant is in the protonated form. .

Interfacial tension at C-W interface. The IFT between CO_2 and 22% TDS brine was measured at 3400 psia and 24-120 °C in the presence of $C_{12-14}N(EO)_2$ with concentrations from $10^{-7.4}$ to $10^{-1.4}$ M (10^{-5} to 1 % w/w) as shown in **Figure 5**. To our knowledge, due to the lack of soluble and stable surfactants in water in previous studies,^{27, 34} interfacial properties of a surfactant in a C-W system have not been reported previously at temperatures above 100 °C. Without surfactant, the IFT ranges from 33 to 44 mN/m from 2500-3900 psia between 25 and 125 °C.³⁶ Upon adding $C_{12-14}N(EO)_2$ with a surfactant concentration above the CMC, the IFT was reduced to 3-5 mN/m at 3400 psia. In the presence of high pressure CO_2 , the low pH (~ 3)⁶⁴ condition in the brine phase ensured the surfactant was in its cationic form, and thus was sufficiently well solvated even at 120 °C to enable IFT measurements. As the temperature increased from 25 to 120 °C the IFT increased from 2.9 to 5.1 mN/m at surfactant concentrations above the CMC.⁶⁶ The reduction of IFT with added surfactant at high temperature suggests CO_2 still solvates the linear alkane tails despite the relatively low CO_2 density of only 0.48 g/mL.⁶⁶

Critical micelle concentration. A discontinuity in the slope of IFT versus log surfactant concentration is evident in **Figure 5** indicating the CMC. The CMC increases about an order of magnitude with an increase in temperature, indicating a preference for the surfactant to stay in the monomeric state in brine as a result of the enhanced monomer solubility in brine.⁶⁶ As temperature increases at constant CO_2 density, the solvation of the protonated nitrogen atom and hydrocarbon tail is improved in brine, which disfavors micellization⁶⁷ (higher CMC) as observed. However, the dissociation of the micelles is hindered somewhat by the reduction in the solvation of two hydroxyethyl groups.⁶⁷ For similar reasons, the CMC of ionic C_{10} and C_{14} alkyl sulfates increases with increasing temperature from 25-70 °C.⁶⁸ To our knowledge, our study is the first to show this trend continues at temperatures above 100 °C.

Adsorption at the C-W interface and efficiency in lowering the interfacial tension (pC_{20}).

The adsorption of $C_{12-14}N(EO)_2$ was determined from the slope of the plot of the IFT versus the log of surfactant concentration (**Equation 6**). At low or moderate temperatures, the reciprocal of the adsorption

at the CO₂-22% TDS brine interface was $\sim 160 \text{ \AA}^2$ per molecule, higher than the value of 200-350 $\text{\AA}^2$ for alkyl EO/PO nonionic surfactants at the C-W interface.²⁷ Generally, ionic surfactants tend to have a lower specific adsorption (higher area per molecule) than nonionic surfactants due to electrostatic repulsion between surfactant head groups.⁵³ However, the highly screened repulsion at high ionic strength led to the high surfactant adsorption at the interface.⁶⁶ Furthermore, the head group for C₁₂₋₁₄N(EO)₂ contains a single nitrogen atom and two hydroxyethyl groups, which is much smaller than the head groups of previously studied nonionic alkyl EO/PO surfactants (for example, with 9 or more EO units^{27,34}) and thus occupies a smaller area.

When temperature was increased at a constant pressure of 3400 psia, the specific adsorption of C₁₂₋₁₄N(EO)₂ at the CO₂-brine interface decreased slightly from $1.05 \times 10^{-6} \text{ mol/m}^2$ at 24 °C to $0.80 \times 10^{-6} \text{ mol/m}^2$ at 120 °C, as shown in **Table 3**. The γ_0 for the binary C-W system increases with an increase in temperature at constant pressure, since the CO₂ density decreases from 0.98 to 0.49 g/ml. A higher IFT (γ_0) alone would provide a greater driving force for surfactant adsorption to the interface.²⁷ However, this contribution was overshadowed by the reduction of CO₂ density and consequently, the weaker tail solvation in CO₂ compared to the strong head solvation, which drove the surfactant towards water. Therefore, the specific adsorption at the interface decreased, but was still quite high indicating significant tail solvation despite the low CO₂ density. In addition, the increased thermal motion also increases the area per surfactant molecule.⁵³

The efficiency of the surfactant was characterized by pC₂₀ for C₁₂₋₁₄N(EO)₂, the negative logarithm of the concentration of surfactant in the bulk phase required to produce a 20 mN/m reduction in interfacial tension. It decreased a small amount from 24 to 120 °C as shown in **Table 3**. When the temperature increases, the contribution from the larger driving force resulting from the larger γ_0 increases³⁶ would drive the surfactant towards the C-W interface, resulting in an increase in pC₂₀.⁶⁹ However, this effect was overcome by the higher tendency of the surfactant to move towards water as explained above. At 24 °C, the pC₂₀ for C₁₂₋₁₄N(EO)₂ for CO₂-22% TDS brine system was ~ 8 which is higher than the calculated value of ~ 5 reported previously for the nonionic surfactant LA-EO₁₂ (C₁₂(EO)₁₂),²⁷ which has a similar tail length (C₁₂). The lower pC₂₀ for LA-EO₁₂ may indicate an HCB value further from unity, given the relatively large EO number of 12 in LA-EO₁₂. The pC₂₀ is expected to increase with increase of alkyl length due to negative free energy of adsorption of a methylene group at the interface.⁵³ However, if the tails become too long, they are not solvated sufficiently well by CO₂ and pC₂₀ is expected to decrease.² A high pC₂₀ in the presence of concentrated brine indicates C₁₂₋₁₄N(EO)₂ had the proper tail length relative to the cationic head group to efficiently lower the IFT of C-W system. In summary, the high surfactant efficiency and strong adsorption at the water-CO₂ interface are very

desirable properties for stabilizing C/W emulsions and foams, despite the extreme temperatures and salinity.

Apparent viscosity of bulk foam and foam in porous media composed of glass beads or crushed calcium carbonate

The remainder of this study addresses the properties of foams, now that the key requirements have been met for phase equilibria and interfacial properties at low pH values from 3 to 4. Here $C_{12-14}N(EO)_2$ is cationic, which enables a high cloud point $>120\text{ }^{\circ}\text{C}$ in brine, whereby micelles are present with a low IFT. The high surfactant solubility in brine is needed to avoid precipitation in the lamellae films of foams. Also, the low C/W partition coefficients favor the formation of C/W foams according to the Bancroft rule. Finally, the low C-W interfacial tension ($\sim 5\text{ mN/m}$) (**Figure 5**) reduces the capillary pressure and thus the tendency for bubble coalescence upon film drainage.

Bulk foam apparent viscosity in a capillary tube. To generate a bulk C/W foam, 1% w/w $C_{12-14}N(EO)_2$ in 22% TDS brine solution at pH 6 (adjusted by adding HCl initially) was injected simultaneously with pure CO_2 into a 76 Darcy calcium carbonate packed bed. The bulk foam apparent viscosity was measured in a $660\text{ }\mu\text{m}$ ID capillary tube downstream of the calcium carbonate foam generator. The effects of temperature and foam quality (CO_2 volumetric fraction) on bulk foam apparent viscosity (μ_{foam}) are shown in **Figure 6**. With an increase of temperature, μ_{foam} decreased from 23.6 cP at $24\text{ }^{\circ}\text{C}$ to 5.7 cP at $120\text{ }^{\circ}\text{C}$ at 90% foam quality, 3400 psia, and a total velocity of 82900 ft/day (0.292 m/s) in the capillary (**Figure 6A**). The temperature affects the apparent foam viscosity in various ways. A decrease of the continuous phase viscosity μ_e with temperature directly contributes to a decrease in the apparent foam viscosity as shown in **Equation 3**. This viscosity reduction in the continuous phase will also lead to more rapid film drainage as shown in **Equation 4**. In addition, γ increases with temperature as a result of the lower density of CO_2 and thus weaker solvation of the surfactant tail (**Figure 5**), which raises P_c and thus raises ΔP_{film} , which will accelerate film drainage for a given bubble size. As the lamellae become too thin, the disjoining pressure becomes insufficient to prevent coalescence. The resulting increase in average bubble size (increased R) causes μ_{foam} to decrease (**Equation 3**).

At $120\text{ }^{\circ}\text{C}$, as the foam quality increased from 70 to 90%, μ_{foam} increased from 2.4 cP to 5.7 cP. μ_{foam} decreased to 1.6 cP at 92% foam quality, and eventually no foam was produced at 95% CO_2 volumetric fraction (**Figure 6B**). With an increase in the foam quality from 70% to 90%, μ_{foam} increases as depicted in Equation 3. Assuming a constant bubble size, this increase in viscosity may be attributed to an increase in the number of lamellae per unit length.⁷⁰ Eventually,

above 90 % foam quality, the lamellae may become too thin to prevent coalescence and a large decrease in μ_{foam} is observed (**Figure 6B**). The highest foam apparent viscosity in the capillary achieved at 90% foam quality was more than 50 times of the baseline apparent viscosity of the CO₂-22% TDS brine mixture without any surfactant present (**Figure S2**).

C/W foam formation and apparent viscosity in a uniform glass bead pack. Given an understanding of bulk foam, we now examine the more complex behavior of foam flow in porous media, whereby the lamellae interact with the pore surfaces.⁷ For bulk foam at a high shear rate in a single capillary, the bubble radius has been found to be smaller than the capillary radius.³ However, in porous media the radius of the bubble is often similar or larger when compared to the pore size indicating only a single aqueous lamella exists in each pore.^{7, 70}

To study foam behavior in porous media, 1% w/w C₁₂₋₁₄N(EO)₂ in a 182 g/l NaCl (model brine without the presence of divalent ions) solution at pH 4 was co-injected with CO₂ at a total superficial velocity from 6 to 181 ft/day. The permeability of the uniform glass bead pack (30 to 50 μ m diameter beads) was 1.2 Darcy as measured with water. As shown in **Figure 7**, at 40% foam quality, the apparent viscosity at a low superficial velocity of 6 ft/day was low, below 3.5 cP. As the velocity increased to 10 ft/day (shear rate of 75 s⁻¹), the apparent viscosity increased markedly to ~150 cP indicating generation of a strong C/W foam. At this low shear rate, foam generation is produced by repeated snap off and lamellae division.⁷ Here, the pressure gradient exceeded the minimum pressure gradient (MPG) need to overcome the capillary forces to mobilize the curved lamellae through the pore throats as described in detail in the supporting information.⁷¹ Upon increasing the total superficial velocity, the MPG for foam generation was found to be 2.7 psi/ft (**Figure S3**) for 40% foam quality. The value of the MPG is consistent with an earlier study of foams at lower temperatures⁷¹ indicating similar generation mechanisms as discussed further in the supporting information. For 80% foam quality, a higher velocity was required to achieve the same pressure gradient (**Figure S3**) and similar apparent viscosity (**Figure 7**).

For both 40% and 80% foam qualities, viscous C/W foams with apparent viscosities above 130 cP were achieved at superficial velocities of 10-20 ft/day (Figure 7). A large decrease in apparent viscosity is observed after the maximum indicating substantial shear thinning. The maximum apparent viscosities in the 1.2 Darcy glass bead pack are an order of magnitude higher than those reported recently for the same surfactant²⁹ in a 30 Darcy sand pack. In the former study, the lower viscosities resulted from shear thinning given the much higher total superficial velocity of 300-600 ft/day (**Figure 7**). The shear thinning behavior may be attributed to bubble deformation and interfacial tension gradient as the bubbles flow through each channel in the porous media, as explained from a model developed by Hirasaki and Lawson for smooth capillaries.⁷⁰ The viscosity in the shear thinning region is proportional to the -0.69

and -1 power of the gas velocity for the 80% and 40% foam quality, respectively. Remarkably, these data are in agreement with the model of Falls et al. (**Equation S23**) where the foam viscosity is proportional to either -2/3 or -1 power the gas velocity at high or low shear rate respectively.⁷²

C/W foam formation and apparent viscosity in 76 Darcy calcium carbonate packed bed. In this final section foam behavior in crushed calcium carbonate is shown to be similar to that in the glass bead pack. These experiments are of great practical interest for foams for enhanced oil recovery in limestone subsurface reservoirs. It is shown below that the Ca^{2+} and Mg^{2+} ions in the inlet brine reduce the dissolution of the CaCO_3 , which maintains a lower pH and thus more protonated surfactant needed for foam formation.

Effect of NaCl and divalent ions. In the crushed limestone pack, foams were not formed when the aqueous phase was DI water (**Figure S4**). Here the surfactant was not sufficiently protonated at 120 °C, as the soluble bicarbonate and carbonate produced a pH of 4.6, according to a geochemical model for the various reaction and phase equilibria, PHREEQC (**Figure S5**). Similarly, the apparent viscosity reached only 8 cP for 60 – 180 g/l NaCl (**Figure S4**). According to the simulations using PHREEQC, the addition of divalent ions such as Ca^{2+} and Mg^{2+} at the concentrations in this study decreased the equilibrium pH of the system from ~4.6 to 3.7 (**Figures S5 and S6**). These ions suppressed the dissolution of CaCO_3 due to the common ion effect. The decrease in pH favored the cationic state of the surfactant needed for foam stabilization. Thus, the addition of divalent ions enhanced the viscosity of the C/W foam from 8 to 14 cP at a quality of 90% (**Table S1**).

Effect of foam quality. The effect of foam quality on apparent viscosity of C/W foam stabilized with $\text{C}_{12-14}\text{N}(\text{EO})_2$ or the analogous quaternary ammonium salt $\text{C}_{12-14}\text{N}(\text{EO})_2\text{CH}_3\text{Cl}$ in a 76 Darcy calcium carbonate packed bed with a total superficial velocity of 938 ft/day is shown in **Figure 8**. For $\text{C}_{12-14}\text{N}(\text{EO})_2$, foam was generated either by co-injection of 1% w/w surfactant at pH6 in a 22% TDS brine solution and CO_2 , or by co-injection of a 0.2 % w/w surfactant - CO_2 solution with a 22% TDS brine solution containing Ca^{2+} and Mg^{2+} without added HCl. When $\text{C}_{12-14}\text{N}(\text{EO})_2$ was injected from the brine phase, as the quality increased from 70% v/v, the apparent foam viscosity increased gradually until it reached a maximum of 14 cP at 90% and then decreased. At 95% CO_2 volumetric fraction, no foam was formed. As the foam quality increases, the size of the pores invaded by the gas phase continually decreases (and so does the water saturation) in the calcium carbonate packed bed, increasing the capillary pressure. Eventually, the van der Waals attraction between CO_2 bubbles exceeds the electrostatic repulsion from the surfactant head groups and the lamellae become unstable.^{73, 74}

When $\text{C}_{12-14}\text{N}(\text{EO})_2$ was injected from the CO_2 phase, the behavior was very similar up to a quality of 90%. At this quality, the experiments were designed such that the concentration of C_{12} .

$_{14}\text{N}(\text{EO})_2$ in the foam (aqueous phase + CO_2 phase) was the same, $\sim 0.16\%$ w/w. The equivalence of foam apparent viscosity indicates that the surfactant underwent effective transport to the interface from either the brine or CO_2 phase, indicating good contact between phases. At 95% foam quality, when the surfactant was injected from the CO_2 phase, the foam apparent viscosity was the highest. In contrast, the surfactant failed to generate foam at 95% foam quality when injected from the aqueous phase. This difference in behavior can be attributed to the difference in surfactant concentration in the total injected fluid. Here, the concentration of $\text{C}_{12-14}\text{N}(\text{EO})_2$ in the total injected fluid was 0.18% when it was injected from the CO_2 phase compared to only 0.10% when injected from the brine phase. This lower concentration was found to provide an insufficient disjoining pressure against the higher capillary pressure at a higher foam quality of 95% resulting in destabilization of the C/W foam.⁷³

For 70 and 90% foam quality, the apparent viscosity was similar for the quaternary ammonium $\text{C}_{12-14}\text{N}(\text{EO})_2\text{CH}_3\text{Cl}$ surfactant as for $\text{C}_{12-14}\text{N}(\text{EO})_2$ with the same tail length, where all other conditions were held constant as depicted in **Figure 8**. Thus, $\text{C}_{12-14}\text{N}(\text{EO})_2$ appeared to behave as a cationic surfactant, consistent with the expected protonation at these conditions. A limitation of the quaternary amine is that it undergoes Hoffman dealkylation at the high temperatures over time. At short times however, it serves as a useful model for the protonated $\text{C}_{12-14}\text{N}(\text{EO})_2$.

To understand the mechanism of foam formation at a high velocity of 939 ft/day and shear rate of $\sim 600\text{ s}^{-1}$, measurements of CO_2 bubble sizes were conducted at room temperature and 90% foam quality. As depicted in **Figure 9A**, the average bubble size was found to be $\sim 20\text{ }\mu\text{m}$. The bubble size distribution shown in the histogram (**Figure 9B**) indicates that $\sim 80\%$ of the bubbles are $30\text{ }\mu\text{m}$ or less. Since this size is clearly smaller than the pore diameter (32 – 65 microns), multiple bubbles were formed in each pore, as a consequence of the high shear rate, as also observed by Adkins et al.³ In contrast, at low shear rates CO_2 bubbles are known to be equal to or larger than the pore diameter.^{7, 70}

Effect of temperature. The effect of temperature on foams at pH 6 in the 76 Darcy calcium carbonate packed bed at foam quality 90% and total superficial velocity 938 ft/day from 24 to 120 °C is shown in **Figure 10**. The apparent viscosity decreased from 36 cP at 24 °C to 14 cP at 120 °C. This decrease can be explained in a similar manner as described for bulk foam (**Figure 6A**). The decrease in viscosity of the aqueous phase with temperature contributes to the decrease in foam apparent viscosity (**Equation S22**).²⁹ This lower viscosity leads to faster film drainage whereby the thinner films more easily rupture resulting in coalescence.^{3, 37, 38, 39} With a smaller number of lamellae per unit length, the apparent viscosity decreases.⁷⁰

Conclusions

A comprehensive study of phase behavior, interfacial properties and CO₂-in-water foam rheology at elevated temperatures up to 120 °C, has been conducted for a switchable (pH – responsive) amine surfactant, C₁₂₋₁₄N(EO)₂. Remarkably, at 120 °C, even with a CO₂ density of only 0.48 g/ml, the tail solvation was sufficient such that the surfactant adsorption at the CO₂-water interface was high, despite the high thermal energy. This work provides a fundamental understanding for a new domain of interfacial science at high temperature and pressure that is of great interest for stabilizing CO₂ foams, even with concentrated brines including divalent ions, which are encountered in subsurface applications including CO₂ storage and EOR. The results support the following conclusions:

1. The solubility of the surfactant in the aqueous phase (cloud point) was measured as a function of temperature up to 120 °C and salinity up to 22%TDS and related quantitatively to the measured degree of protonation. The cloud point was >120 °C at a degree of protonation greater than 0.8. This solubility at such a high temperature and salinity is rarely encountered for anionic and nonionic surfactants previously reported in literature.^{18, 23}
2. Previous studies of the interfacial behavior of switchable amine surfactants have been limited to air – water and oil – water interfaces at room temperature.⁷⁵ In this paper, the interfacial behavior of such surfactants was extended to the CO₂ – water interface at high temperature up to 120 °C. Properties such as interfacial tension, critical micelle concentration (CMC) and adsorption of the surfactant at the C-W interface as a function of temperature were explained in terms of the interactions of the surfactant tail and head with the CO₂ and aqueous phase, respectively. Here, C₁₂₋₁₄N(EO)₂ was effective in lowering the interfacial tension (~40 to ~5 mN/m) with high adsorption at the C-W interface even at 120 °C. The surfactant adsorption of ~200 Å²/molecule and surfactant efficiency did not decrease significantly as the temperature was increased from room temperature to 120 °C given the increase in γ_0 that was balanced by a modest weakening in surfactant tail solvation. The adsorption of C₁₂₋₁₄N(EO)₂ was higher than previously reported for nonionic surfactants at temperatures that did not exceed 70 °C.^{27, 34} The higher adsorption of C₁₂₋₁₄N(EO)₂ may be attributed in part to the smaller headgroup of C₁₂₋₁₄N(EO)₂ relative to those of the nonionic surfactants with similar tails.
3. The understanding of phase behavior and interfacial properties of C₁₂₋₁₄N(EO)₂ at high temperature provided a basis for the study of formation, stability and rheology of CO₂-water emulsions and foams with switchable amine surfactants. Emulsions and dispersions for such surfactants have been often limited to oil – water emulsions.^{40, 41} With C₁₂₋₁₄N(EO)₂, foam was generated successfully in a capillary tube and in two types of porous media. For bulk foams in a capillary tube, the decrease in apparent viscosity with an increase in temperature may be attributed to faster drainage of the lamellae

due to a decrease in the continuous phase viscosity and a greater capillary pressure, given the higher interfacial tension. Despite these changes, the apparent viscosity of 5.7 cP at 120 °C was more than 50 times of the apparent viscosity of CO₂-brine mixture without surfactant at the same conditions. Foams at such high temperature and salinity are rarely encountered in literature due to limitations in aqueous solubility, thermal stability and defoaming effects at these severe conditions.^{76, 77}

4. C₁₂₋₁₄N(EO)₂ also stabilized foams in porous glass bead packs and crushed calcium carbonate media. With only 1 % w/w C₁₂₋₁₄N(EO)₂ in brine, C/W foams were formed at low superficial velocities with an apparent viscosity up to 146 cP which is an order of magnitude higher than reported previously for the same surfactant.²⁹ The viscosity increase is explained in terms of shear thinning behavior of foams in porous media consistent with previously developed rheological models.^{70, 72} For calcium carbonate media, stable foams could be formed by suppressing the dissolution of CaCO₃ by adding Ca²⁺ and Mg²⁺ in the aqueous phase (via the common ion effect) in order to maintain a low enough pH to protonate the surfactant. This fundamental understanding of interfacial phenomena at high temperatures as well as the properties of foams is of interest for a variety of applications including CO₂ enhanced oil recovery at novel conditions of high temperature and salinity and CO₂ sequestration.

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Author contribution

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Supporting information

Supporting information available: theory of bulk foam apparent viscosity and stability (continued); potentiometric titration for determination of the degree of protonation; apparatus for apparent viscosity measurement; PHREEQC simulation (continued); effect of CO₂ pressure on simulated pH of effluent at 120 °C in the presence of 22% TDS brine and excess calcium carbonate; Effect of foam quality on apparent viscosity of CO₂/brine mixture without surfactant in a 76 Darcy crushed calcium carbonate packed bed and a downstream capillary tube (660 μm ID) at 120 °C, 3400 psia, total superficial velocity 938 ft/day in calcium carbonate packed bed; effect of total superficial velocity on the pressure gradient in 1.2 Darcy glass bead pack by injecting 1% w/w C₁₂₋₁₄N(EO)₂ 182 g/L NaCl brine pH 4 solution with CO₂ at 40% or 80% foam

quality at 120 °C, 3400 psia; minimum pressure gradient for foam generation; smooth capillaries model and shear thinning in porous media; effect of initial concentration of Ca^{2+} or Mg^{2+} on simulated pH at equilibrium at 120 °C, 3400 psia in the presence of excess calcium carbonate and CO_2 ; apparent viscosity of C/W foam stabilized with 1% w/w $\text{C}_{12-14}\text{N}(\text{EO})_2$ 22%TDS brine or 182 g/L NaCl brine solution; pH of aqueous phase was adjusted to 6 by HCl initially. 120 °C, 3400 psia, total superficial velocity 938 ft/day in a 76 Darcy calcium carbonate packed bed with foam quality from 70% to 95%.

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Figures and tables

Table 1. Cloud point temperatures of 1% w/w C₁₂₋₁₄N(EO)₂ aqueous solution versus salinity and temperature (adjusted with HCl). The uncertainty in the cloud point temperature is ± 1 °C.

pH	Salinity			
	0	120 g/L NaCl	182 g/L NaCl	22% TDS
4.0	>120	>120	>120	>120
5.5	-	>120	-	>120
6.0	90	110	-	>120
6.5	-	100	-	80
7.0	Insoluble	Insoluble	Insoluble	Insoluble

Table 2. Partition coefficients of C₁₂₋₁₄N(EO)₂ (weight fraction in CO₂/weight fraction in brine) between CO₂ and brine with gentle stirring at 25-90 °C, 1000 or 3400 psia. (CO₂ and brine were equal in mass. 0.25 % (w/w) surfactant in total mass of CO₂ and brine

Salinity	Temperature (°C)	Pressure (psia)	Density of CO ₂ (g/mL)	Average partition coefficient
182 g/L	24	3400	0.94	0.030 ± 0.010
NaCl	60	3400	0.77	0.030 ± 0.0010
	90	3400	0.61	0.032 ± 0.0010
22% TDS	24	3400	0.94	0.026 ± 0.0040
	90	3400	0.61	0.028 ± 0.0020
	90	1000	0.12	<0.0040

Table 3. Interfacial properties of C₁₂₋₁₄N(EO)₂ at the CO₂-22% TDS brine interface at 3400 psia. Error in interfacial tension measurements is less than 4%.

T	$\rho(\text{CO}_2)$	CMC	CMC	IFT _{cmc}	π_{cmc}	Γ^*10^6	A _m	pC ₂₀
(°C)	(g/mL)	(% w/w)	(mmol/L)	(mN/m)	(mN/m)	(mol/m ²)	(Å ² /molecule)	
24	0.94	0.00016	0.0070	2.9	34-37	1.1	158	7.6-8.1
90	0.61	0.00053	0.022	3.7	-	0.90	184	-
120	0.48	0.00094	0.038	5.1	35-39	0.80	207	6.9-7.6

Figure 1. Effect of formulation variables on the phase behavior and interfacial tension of CO₂-water-ionic surfactant system.

Figure 2. Apparatus for CO₂-water foam viscosity measurements in porous media and in a capillary tube. BPR : back pressure regulator. PT: pressure transducer. A glass bead pack or crushed calcium carbonate packed bed is used as the foam generator.

Figure 3. Degree of protonation of $C_{12-14}N(EO)_2$ (1% w/w) vs pH at 1 atm.: (A) 22% TDS brine at 24 ($\diamond$), 50 (Δ) and 90 ($\circ$) °C. (B) DI water (no salt) ($\diamond$), 120g/L NaCl brine (Δ) or 22% TDS brine ($\circ$) at 90 °C. (Phase boundaries where the solution became clear upon lowering pH are marked with red circles.

Figure 4. Partition coefficients of $C_{12-14}N(EO)_2$ (weight fraction in dodecane/weight fraction in brine) between dodecane and 22%TDS brine at 25 °C, and 1 atm. (Dodecane and brine were equal in volume. 1 % (w/w) surfactant in 22%TDS brine. The inset indicates the type of emulsion from conductivity measurements, O/W at pH 7.5 and W/O at pH 8.2.

Figure 5. Interfacial tension (IFT) for $C_{12-14}N(EO)_2$ at the CO_2 -22%TDS brine interface versus the logarithm of surfactant concentration. The intersection of the curves denotes the critical micelle concentration (CMC). The pH of the aqueous phase is ~ 3 (see reference 48).

A

B

Figure 6. Apparent viscosity of bulk foam in the capillary tube stabilized with 1% w/w $C_{12-14}N(EO)_2$ 22% TDS brine at pH 6 (adjusted by adding HCl) solution with a total velocity 82900 ft/day at 3400 psia. (Foam was generated in a 76 Darcy calcium carbonate pack): (A) Effect of temperature at foam quality of 90%; (B) Effect of foam quality at 120 °C.

Figure 7. Apparent viscosity of C/W foam stabilized with $C_{12-14}N(EO)_2$ at 3400 psia and 120 °C by co-injecting 1% (w/w) $C_{12-14}N(EO)_2$ in 182 g/l NaCl brine pH 4 solution with pure CO_2 in either a 1.2 Darcy glass bead pack or 30 Darcy sand pack at 40% or 80% foam quality.

Figure 8. Apparent viscosity of C/W foam stabilized at 3400 psia, 120 °C, and total superficial velocity of 938 ft/day in 76 Darcy calcium carbonate packed bed by coinjecting 1%(w/w) surfactant in 22%TDS brine solution with pure CO_2 or 0.2% (w/w) surfactant in CO_2 solution with 22%TDS brine.

A

B

Figure 9. A) Micrograph of C/W foam stabilized at 3400 psia, 25 °C and 90% foam quality by co-injecting 1% (w/w) $C_{12-14}N(EO)_2$ 22%TDS brine pH 6 solution with CO_2 , with a total superficial velocity 938 ft/day in 76 Darcy calcium carbonate pack. B) Histogram of bubble size distribution.

Figure 10. Apparent viscosity of C/W foam stabilized at 3400 psia and 90% foam quality by co-injecting 1% (w/w) $C_{12-14}N(EO)_2$ 22%TDS brine pH 6 solution with CO_2 at 24-120 °C, with a total superficial velocity 938 ft/day in 76 Darcy calcium carbonate pack.

Graphical abstract