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## Switchable diamine surfactants for CO<sub>2</sub> mobility control in enhanced oil recovery and sequestration

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### Abstract

The design of switchable amine surfactants for CO<sub>2</sub> EOR in carbonate reservoirs at high temperatures is challenging because of the increase in the pH due to dissolution of calcium carbonate at acidic conditions. The increased pH hinders the protonation of the surfactant and its aqueous solubility. In this work, the addition of a second amine headgroup ensured that C<sub>16-18</sub> N(EO)C<sub>3</sub>N(EO)<sub>2</sub> is soluble in 22%TDS brine at neutral pH conditions. Also, captive bubble tensiometry measurements confirmed the activity of the surfactant at the C-W interface by large reduction in the interfacial tension coupled with high adsorption. Also, the surfactant generated viscous foam that can stabilize the displacement front in CO<sub>2</sub> EOR processes and decrease the mobility of CO<sub>2</sub> for enhanced CO<sub>2</sub> sequestration.

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## 1. Introduction

Carbon dioxide is considered the primary contributor to the increase in the levels of greenhouse gases in the atmosphere causing a concern about climate change.[1] CO<sub>2</sub> emissions reduction can be accomplished by a shift from fossil fuels to renewable energy resources or a decrease in the CO<sub>2</sub> intensity of fossil fuels. Alternatively, the most promising option is long term storage of CO<sub>2</sub> in underground formations.[2] The global potential capacity for storage of CO<sub>2</sub> as is sufficient to store emitted CO<sub>2</sub> for several decades underground for hundreds of years.[3] Carbon dioxide enhanced oil recovery (CO<sub>2</sub> EOR) is a technology that increases oil production using CO<sub>2</sub> with opportunity of CO<sub>2</sub> storage underground.[4, 5] Oil reservoirs in particular are attractive CO<sub>2</sub> sinks owed to their geological seals that can cap liquids and gases for a long time.[5] Injection of CO<sub>2</sub> for the purpose of enhanced oil recovery (CO<sub>2</sub> EOR) coupled with CO<sub>2</sub> sequestration can be an economically feasible where the cost of CO<sub>2</sub> is offset by the profits gained from oil production.[4]

One of the main challenges during CO<sub>2</sub> EOR that affects oil production and CO<sub>2</sub> storage is the early breakthrough of CO<sub>2</sub> due to its physical properties.[6] CO<sub>2</sub> has low viscosity relative to the targeted oil causing viscous fingering and low oil recovery.[6] Also, the low density of CO<sub>2</sub> results in gravity override where CO<sub>2</sub> rises to the top parts of the porous media without contacting the targeted oil.[6] Mitigation of these issues can be achieved by the addition of small amounts of amphiphiles such as surfactants to generate CO<sub>2</sub> in water (C/W) macroemulsions (foams).[7] C/W foams consist of CO<sub>2</sub> bubbles dispersed in a continuous aqueous phase yielding viscosities that are orders of magnitude greater than that of pure CO<sub>2</sub>. [8] Surfactant phase behavior between water and CO<sub>2</sub> is essential in determining the type of emulsion generated. For the preferred C/W macroemulsions, surfactants with a hydrophilic/CO<sub>2</sub>-philic balance (HCB) of greater than unity are selected.[9] Here, the surfactant head group interactions with water are greater than those of the surfactant tail with CO<sub>2</sub>. [9] In addition, surfactants must reduce the interfacial tension (IFT) to lower the energy requirement for creation of new interfaces and generation of stable foams.[10]

Very few studies attempted to design surfactants for high temperature CO<sub>2</sub> EOR applications in carbonate reservoirs because of the limited aqueous solubility and stability of surfactants at elevated temperatures. For example, nonionic surfactants usually exhibit cloud points above 100 °C because of the diminished hydrogen bonding that causes micelles to aggregate.[11] Although anionic surfactants such as sulfates and sulfonates can generate foam at high temperatures they adsorb strongly on positively charged carbonate reservoirs at CO<sub>2</sub> flooding conditions.[12] Chen et al. utilized switchable ethoxylated amine surfactant C<sub>12-14</sub>N(EO)<sub>2</sub> to stabilize C/W foam at temperatures up to 120 °C in different porous media.[13, 14] The cationic form of the surfactant was soluble in 22%TDS brine at that temperature because of the strong ionic dipole interaction between the protonated amine head and water.[13]

The objective of this paper is to demonstrate that a switchable diamine surfactant C<sub>16-18</sub>N(EO)C<sub>3</sub>N(EO)<sub>2</sub> is water soluble in 22%TDS brine at neutral pH up to 120 °C. A study of the degree of protonation will be conducted to examine the switchability of the surfactant as a function of pH and salinity. Furthermore, C-W interfacial tension measurements at high temperature up to 120 °C will be used to calculate interfacial properties such as the critical micelle concentration (CMC) and surfactant adsorption at the C-W interface. These interfacial properties will be compared to a previously reported surfactant C<sub>12-14</sub>N(EO)<sub>2</sub> to demonstrate the effect of the additional amine in the surfactant head and the longer tail. Finally, it will be demonstrated that C<sub>16-18</sub>N(EO)C<sub>3</sub>N(EO)<sub>2</sub> can generate viscous C/W foams at 120 °C in crushed carbonate minerals. The effect of foam quality (fractional flow of CO<sub>2</sub>) on foam viscosity will be explained in terms of lamella density, capillary and disjoining pressures.

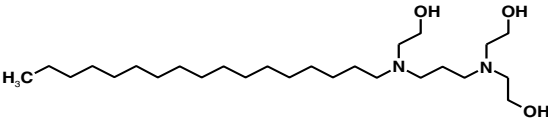
## 2. Experimental

### 2.1. Materials

Tris(2-hydroxyethyl)-N-tallowalkyl-1,3-diaminopropane (Ethoduomeen T/13) was a gift from Akzo Nobel and used without further purification. The structure of the surfactant is shown in **Table 1**. Carbon dioxide (Matheson, Coleman grade, 99.99%) was used as received. Sodium chloride (NaCl, certified ACS, Fisher), calcium chloride dehydrate (CaCl<sub>2</sub>·2H<sub>2</sub>O, 99+% Acros), magnesium chloride hexahydrate (MgCl<sub>2</sub>·6H<sub>2</sub>O, Fisher), hydrochloric acid

(HCl, technical, Fisher) and isopropanol (certified ACS plus, Fisher) were used as received. 22% TDS brine was prepared from deionized (DI) water (Nanopure II, Barnstead, Dubuque, IA) and of 182 g/L NaCl, 77 g/L CaCl<sub>2</sub>·2H<sub>2</sub>O, 26 g/L MgCl<sub>2</sub>·6H<sub>2</sub>O. This brine was used as model reservoir brine. In some experiments, the initial pH of surfactant solution was adjusted by adding HCl.

Table 1 Structure and HLB of Ethomeen T/13

Surfactant	Structure	HLB Davis scale
Ethodumeen T/13		19

## 2.2. Cloud point temperature

Cloud point measurements for 1 wt% surfactant solutions were performed in 22%TDS brine at different pH conditions. The experiments were conducted using sealed glass tubes in an oil bath as outlined in a previous publication.[13]

## 2.3. Potentiometric titration

Solutions of 40 mM C<sub>16-18</sub>N(EO)C<sub>3</sub>N(EO)<sub>2</sub> in DI water or 22%TDS brine mixtures were titrated using 800 mM HCl solution at 90 °C. The surfactant solution was placed in a three neck flask with a magnetic stir bar. The flask was then placed in an oil bath heated with a stirring hot plate with a temperature controller (Corning PC-420D) to maintain the temperature at 90 °C. Mettler Toledo FG2 FiveGo pH meter with pH/ATC electrode was used to measure pH of the solution. A reflux condenser was used to minimize water losses. Volume of added HCl and pH were recorded.

The overall degree of protonation ( $\theta$ ) was calculated by performing a charge balance on the solution (assuming ideal solution) and is given by **Equation 1**

$$\theta = \frac{C_a \times V_{\text{titrant}} + (C_{\text{OH}^-} - C_{\text{H}^+}) \times V_{\text{titrand}}}{C_{\text{total}} \times V_{\text{titrand}_0}} \quad (1)$$

where  $C_a$  is the concentration of HCl and  $C_{\text{H}^+}$  and  $C_{\text{OH}^-}$  are the concentration of H<sup>+</sup> and OH<sup>-</sup> determined from the pH of the solution.  $C_{\text{total}}$  is the total concentration of the unprotonated amine added initially (40 mM).  $V_{\text{titrand}_0}$  is the volume of the amine solution before adding HCl, whereas  $V_{\text{titrand}}$  is the total volume of titrand at any stage of titration.

## 2.4. Interfacial tension measurements at the CO<sub>2</sub>-brine interface

Interfacial tension between CO<sub>2</sub> and aqueous surfactant solution was obtained by analyzing a captive bubble using an axisymmetric drop analysis as described in a previous publication.[15] In this study temperature measurements were extended to 120 °C. Gibbs adsorption equation (**Equation 2**) was used below the CMC to determine the molar surface density of the surfactant monolayer.

$$\Gamma = -\frac{1}{RT} \left( \frac{\partial \gamma}{\partial \ln C_{\text{surf}}} \right)_{T,P} \quad (2)$$

Where  $C_{\text{surf}}$  is the surfactant concentration. The area occupied by each surfactant molecule can be calculated from **Equation 3**

$$A_m = \frac{1}{N_A \Gamma} \quad (3)$$

where  $N_A$  is Avogadro's number.

### 2.5. CO<sub>2</sub> in water foam formation and apparent viscosity

The procedure for foam formation is described in a recent publication.[14] Permeability of the sand pack was calculated from one phase Darcy's law with DI water and was found to be 76 Darcy.

## 3. Results and discussion

### 3.1. Cloud point temperatures

Surfactants with oxyethylene units (EO) often display cloud points due to the dehydration of the head group when hydrogen bonds are weakened at elevated temperature resulting in micellar aggregation.[11] The cloud point temperature as a function of pH was measured for 1 wt% C<sub>16-18</sub>N(EO)C<sub>3</sub>N(EO)<sub>2</sub> in 22%TDS brine as shown in **Figure 1**. Upon the decrease in pH from 7.9 to 7 the cloud point was shown to increase to >120 °C. This enhanced water solubility is due to the increase in the degree of protonation of the surfactant and improved ionization of the two nitrogen atoms that causes an electrostatic repulsion between micelles hindering their aggregation.[11] When compared to previously reported amine surfactant C<sub>12-14</sub>N(EO)<sub>2</sub>, the diamine head of C<sub>16-18</sub>N(EO)C<sub>3</sub>N(EO)<sub>2</sub> enhanced the brine solubility of the surfactant by increasing the required pH for solvation by one unit. Despite the slightly longer tail, C<sub>16-18</sub>N(EO)C<sub>3</sub>N(EO)<sub>2</sub> enhanced solubility is attributed to the added hydrophilicity attained by the additional cationic amine in the head.

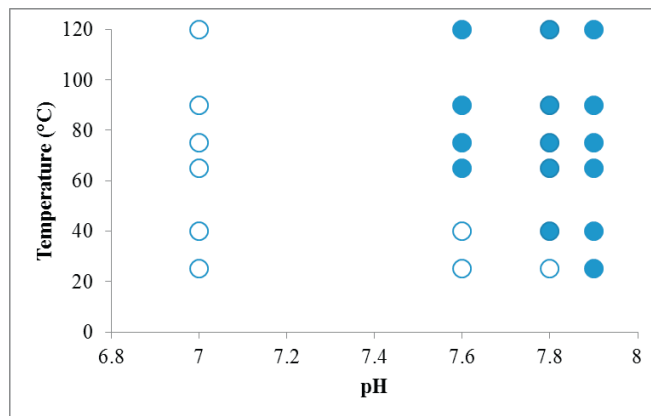
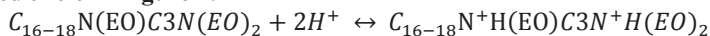


Fig. 1. Water solubility of 1wt% C<sub>16-18</sub>N(EO)C<sub>3</sub>N(EO)<sub>2</sub> in 22%TDS brine. Open circles indicate a clear solution and filled circles indicate cloudy solutions

### 3.2. Effect of salinity on the degree of protonation

The degree of protonation of 40 mM C<sub>16-18</sub>N(EO)C<sub>3</sub>N(EO)<sub>2</sub> at 90 °C in either DI water or 22%TDS is shown in **Figure 2**. With the addition of HCl, long tail alkyl amine surfactants can switch from nonionic form that is insoluble in water to a soluble cationic form according to the reaction below. The pH at which the surfactant solution becomes clear is indicated by a red circle in **Figure 2**.



It was observed that the degree of protonation increases with the increase in salinity at constant pH. For example at pH 5 the degree of protonation of C<sub>16-18</sub>N(EO)C<sub>3</sub>N(EO)<sub>2</sub> increased from ~0.25 to ~0.75 in DI water and 22%TDS,

respectively. At such concentrations (40 mM) surfactants are mainly in micellar form with a partial positive charge on the surface. As a result, positively charged hydronium ions are repulsed from the micelle to inhibit protonation. The addition of  $\text{Cl}^-$  ions screens this electrostatic repulsion to facilitate protonation. An analogous mechanism was given to explain the exclusion of chloride ions from anionic micelles.[16]

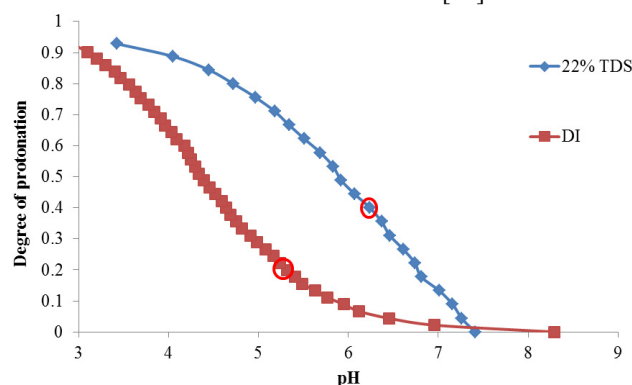


Figure 2. Degree of protonation of  $\text{C}_{16-18}\text{N}(\text{EO})\text{C}_3\text{N}(\text{EO})_2$  vs pH at 40 mM in DI water or 22% TDS brine at 90 °C and 1 atm.

### 3.3. Interfacial properties at the $\text{CO}_2$ – brine interface

Interfacial tension measurements between 22%TDS and  $\text{CO}_2$  were conducted as a function of  $\text{C}_{16-18}\text{N}(\text{EO})\text{C}_3\text{N}(\text{EO})_2$  concentration at 120 °C and 3400 psia. At these conditions the pH is  $\sim 3$ [17] and the surfactant is expected to be completely protonated (cationic) as observed in **Figure 2**. The concentration of surfactant was varied from  $2.63 \times 10^{-7}$  M to  $2.63 \times 10^{-2}$  M. **Figure 3** shows the IFT versus log surfactant concentration and a discontinuity in the slope indicates the presence of a critical micelle concentration (CMC) that has a value of 0.015mM. Furthermore, above the CMC, effective reduction of the IFT was achieved as it decreased from 35 mN/m in the absence of surfactant[18] to 6.2 mN/m. The molar surface density and other interfacial properties of  $\text{C}_{16-18}\text{N}(\text{EO})\text{C}_3\text{N}(\text{EO})_2$  and  $\text{C}_{12-14}\text{N}(\text{EO})_2$  at the  $\text{CO}_2$ -brine interface are compared in **Table 2**. As expected,  $\text{C}_{16-18}\text{N}(\text{EO})\text{C}_3\text{N}(\text{EO})_2$  showed lower adsorption at the interface (higher area per molecule) when compared to  $\text{C}_{12-14}\text{N}(\text{EO})_2$  due to the additional amine in the head that occupies larger area at the interface.[10] Also, **Table 2** shows that the CMC of  $\text{C}_{16-18}\text{N}(\text{EO})\text{C}_3\text{N}(\text{EO})_2$  is half of that of  $\text{C}_{12-14}\text{N}(\text{EO})_2$ . Generally, for ionic surfactants increasing the tail length by a methyl group decreases the CMC by half.[10] On the other hand, the addition of another hydrophilic group to the head increases the CMC by disfavoring micellization.[10] The results obtained suggest that the structural effect of increasing the tail length on the CMC is more profound.

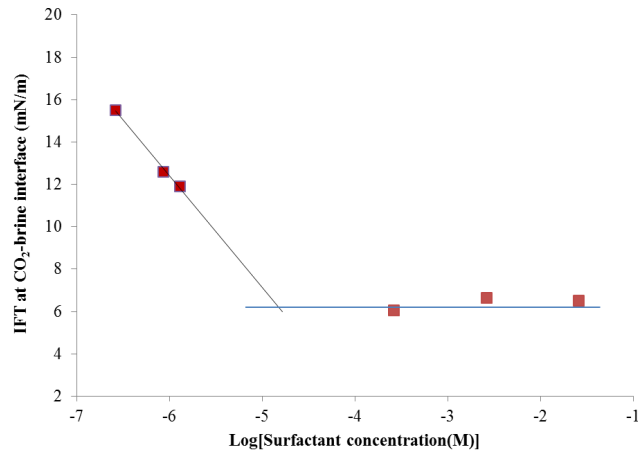


Figure 3. The interfacial tension (IFT) for  $C_{16-18}N(EO)C_3N(EO)_2$  at the  $CO_2$ -22%TDS brine interface at 120 °C and 3400 psia is plotted as a function of the logarithm of surfactant concentration

Table 2 The interfacial properties of  $C_{12-14}N(EO)_2$  and  $C_{16-18}N(EO)C_3N(EO)_2$  at the  $CO_2$ -22% TDS brine interface at 120 °C and 3400 psia

Surfactant	$CO_2$ density (g/mL)	$IFT_{cmc}$ (mN/m)	CMC (mmol/L)	$\Gamma^*10^6$ (mol/m <sup>2</sup> )	$A_m$ (Å <sup>2</sup> /molecule)
$C_{16-18}N(EO)C_3N(EO)_2$	0.476	6.2	0.015	0.70	238
$C_{12-14}N(EO)_2$	0.476	5.1	0.038	1.0	207

### 3.4. Apparent viscosity in 76 Darcy calcium carbonate pack

The effect of foam quality on the apparent viscosity of C/W foams generated in a 76 Darcy calcium carbonate pack is presented in **Figure 4**. It is evident that increasing the foam quality from 60% to 95% results in an increase in apparent viscosity from 5 cP to 14 cP. Assuming a constant bubble size, increasing the foam quality increases the lamella density (number of lamellae per unit length) adding more resistance to flow and increasing the viscosity of the foam.[19] However, at foam quality of 98% no foam was observed as indicated by the low viscosity of only 0.6 cP. Raising the  $CO_2$  fractional flow decreases the radius of curvature of the water meniscus connecting two sand grains resulting in an increase in the capillary pressure.[20] Ultimately, a limiting capillary pressure that overcomes disjoining pressure is achieved and lamellae are ruptured causing an abrupt decrease in the viscosity.

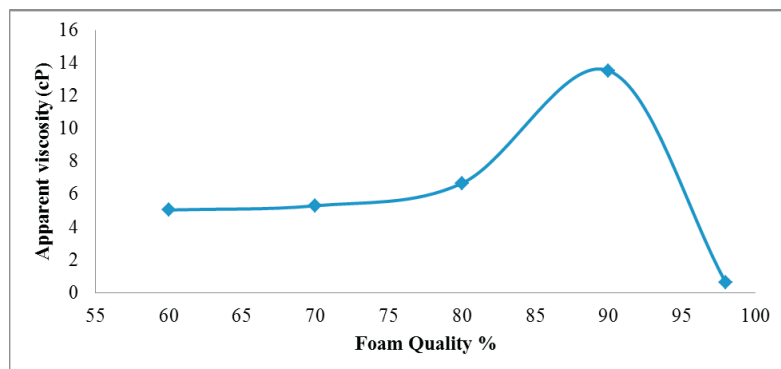


Figure 4. Apparent viscosity of C/W foam stabilized by co-injecting 1% (w/w)  $C_{16-18}N(EO)C_3N(EO)_2$  or 22%TDS brine pH 6.5 solution with  $CO_2$ , at 120 °C, 3400 psia and total superficial velocity 938 ft/day in 76 Darcy limestone pack with foam quality from 60% to 90%

#### 4. Conclusion

The addition of a second cationic amine head to switchable tertiary amine surfactants resulted in an increase in the required pH for aqueous solubility.  $C_{16-18}N(EO)C_3N(EO)_2$  was found to have a cloud point temperature of >120 °C at neutral pH which is one pH unit higher than that of  $C_{12-14}N(EO)_2$  reported previously. The higher pH is essential in ensuring that the surfactant is soluble throughout the  $CO_2$  EOR process even in relatively high pH encountered in carbonate reservoirs. Also, potentiometric titration confirmed that the surfactant can effectively switch from nonionic to cationic forms with high degree of protonation (>80%) at pH values less than 5. The addition of 22%TDS resulted in a substantial enhancement in the degree of protonation of the surfactant owed to the decrease of the repulsion of hydronium ions by the partially cationic micelles. Moreover, the enhanced aqueous solubility enabled interfacial tension measurements at high temperatures at 120 °C.  $C_{16-18}N(EO)C_3N(EO)_2$  was highly effective in lowering the interfacial tension above the CMC to ~6 mN/m. Also, the longer tail of  $C_{16-18}N(EO)C_3N(EO)_2$  compared to  $C_{12-14}N(EO)_2$  resulted in a decrease in the CMC by a factor of 2. Finally, the aforementioned properties enabled  $C_{16-18}N(EO)C_3N(EO)_2$  to generate viscous foam at 120 °C in crushed carbonate minerals. Viscous foam reduces the mobility of  $CO_2$  for stable displacement front and better  $CO_2$  EOR and storage. The foam was most viscous at 90% quality (14cP) and collapsed at 98% quality because the limiting capillary pressure was achieved.

#### Acknowledgement

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