

ORIGINAL ARTICLE

Foaming and defoaming properties of CO₂-switchable surfactants

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Abstract

The present study is about the foaming and defoaming properties of the CO₂-switchable surfactant N,N-dimethyltetradecylamine (C₁₄DMA) and its advantages compared with the non-switchable counterpart tetradecyltrimethylammonium bromide (C₁₄TAB). In the absence of CO₂, C₁₄DMA is a water insoluble organic molecule without any surface activity thus being unable to stabilize foams. In the presence of CO₂, the head group becomes protonated which transforms the water insoluble molecule into a cationic surfactant. Comparing the surface properties and foamability of C₁₄DMA and C₁₄TAB one finds a very similar behavior. However, the foam stabilities differ depending on the gas. Foaming the two-surfactant solutions with CO₂ leads to very unstable foams in both cases. However, foaming the two surfactant solutions with N₂ reveals the switchability of C₁₄DMA: while the volume of foams stabilized with C₁₄TAB hardly changes over 1600 s, the volume of foams stabilized with C₁₄DMA decreases significantly in the same period of time. This difference is due to the fact that the surface activity, that is, the amphiphilic nature, of C₁₄DMA is continuously switching off since CO₂ is displaced by N₂ thus deprotonating and deactivating the surfactant.

KEYWORDSCO₂-switchable surfactants, defoamer, foams, surface properties

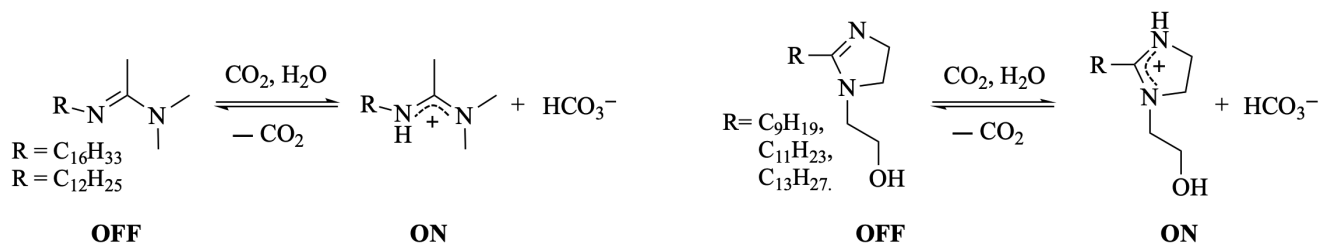
INTRODUCTION

Aqueous foams are widely used in several different industries such as cosmetics, detergents, food, fire-fighting, textiles, foam flooding, and foam flotation (Weaire & Hutzler, 1999). They consist of gas bubbles dispersed in an aqueous phase. In industry, both foam formation and foam decay are crucial steps for smooth processing. To control undesired foam, antifoaming and/or defoaming agents are traditionally used (Hilberer & Chao, 2012; Rao, 2004). Unfortunately, these additives hinder the regeneration of foam, that is, the surfactant solution cannot be reused and becomes harmful aqueous chemical waste since surfactants are toxic to aquatic organisms (Arthur et al., 2012). In foam flooding and foam flotation this chemical waste gets stored in tailing ponds that can be as large as 18 km long and 88 m deep, such as the Syncrude Tailing

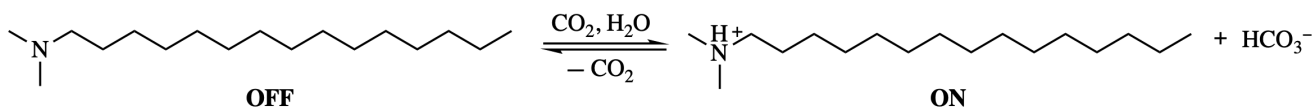
Dam in Fort McMurray, Alberta, Canada (Weber, 2014). These ponds are getting so large that they are having difficulties containing the million cubic meters of chemical waste that are stored in them. It has been estimated that on average, worldwide, there is one big accident involving a tailing pond each year (Diamond, 2005). The mining and petroleum industries use aqueous foams as major processing steps. In order to minimize the amount of chemical waste, one needs systems which allow (i) the foam to be destroyed on demand and (ii) the foaming solution to be reused. One promising possibility to achieve these goals is to use CO₂-switchable surfactants which can be switched between a foam-stabilizing surfactant and a molecule that cannot stabilize a foam at all with the presence or absence of CO₂. CO₂ is an advantageous trigger as it is benign, inexpensive, and does not accumulate in the system (Jessop & Cunningham, 2021).

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SCHEME 1 Switching of the CO₂-switchable cationic surfactants (left) alkyl acetamidines and (right) 2-alkyl-1-hydroxyethylimidazoline (HEAI)



SCHEME 2 Switching of the CO₂-switchable cationic surfactant C₁₄DMA

The largest class of CO₂-switchable surfactants is called “switchable cationic surfactants” (SCSs). SCSs have a switchable basic head group and a non-switchable hydrophobic tail. In the absence of CO₂, the head group is uncharged and hydrophobic, making the OFF form of the molecule. This form of the molecule has little or no surface activity and is thus unable to stabilize foams. In the presence of CO₂, the polar head group becomes protonated, resulting in a cationic surfactant with a bicarbonate counterion. This form of the molecule is the ON form, which has an increased surface activity and is thus able to stabilize foams. Liu et al. first reported a CO₂-responsive surfactant, namely a long-chain alkyl amidine (Liu et al., 2006), that switched ON and OFF solely with CO₂ addition and removal. In the presence of CO₂ and water, the long-chain alkyl amidine is protonated into a charged amidinium bicarbonate surfactant, which has excellent surface activity (Scheme 1, left). When CO₂ is removed from the system, the pH of the solution increases thus deprotonating the amidinium bicarbonate and converting the molecule back to its neutral alkyl amidine form. This surfactant was used for switching emulsion stability (Liu et al., 2006).

CO₂-switchable surfactants have been previously shown to also stabilize or destabilize foams with the addition or removal of CO₂. One of the first to study the foaming properties of CO₂-switchable surfactants was Lu et al., 2014, who studied the foaming properties of 2-alkyl-1-hydroxyethylimidazolines (HEAI) in water (Lu et al., 2014). Under air, HEAI is an organic molecule with poor water solubility and is thus unable to generate and stabilize foams. When CO₂ is added to the solution, the molecule transforms to 2-alkyl-1-hydroxyethylimidazolium bicarbonate (HEAIB), a cationic surfactant with increased water solubility, surface activity and the ability to stabilize foams (Scheme 1, right). The generated foam is then destabilized upon exposure to air or nitrogen. Since 2014, other researchers have used CO₂-responsive

surfactants for switching foam stability. A large focus of these publications has involved CO₂-responsive surfactants for CO₂ flooding in the petroleum industry (Da et al., 2018; Li et al., 2015; Li et al., 2017; Su et al., 2018; Sun et al., 2019; Tang et al., 2018; Wang et al., 2018; Wang et al., 2019; Zhang et al., 2019; Zhang et al., 2020). CO₂ gas is injected into reservoirs to improve oil recovery due to its miscibility with crude oil (Zhang et al., 2018). However, due to its high mobility and low density, CO₂ gas can lead to severe gas channeling and breakthrough, decreasing the efficiency of CO₂. Thus, CO₂ foams have been utilized as they can enter the high permeability zones, impose high flow resistance, and then promote CO₂-fluid diversion to low-permeability zones (Li et al., 2010).

In this study we systematically study the influence of CO₂ and N₂ on foams stabilized with the CO₂-switchable surfactant N,N-dimethyltetradecylamine (C₁₄DMA). At first we tested N'-dodecyl-N,N-dimethylacetimidamide (Scheme 1, left) but found that hydrolysis of the amidine group was fast enough to interfere with measurements (see Data S1), so we instead focused on the tertiary amine C₁₄DMA which does not suffer from hydrolysis and has the additional advantage of switching OFF more quickly once CO₂ is removed (Fowler et al., 2012). We will show that C₁₄DMA is as good a foaming agent as its non-switchable counterpart tetradecyl trimethylammonium bromide (C₁₄TAB) but that it can be switched OFF with an external trigger (Scheme 2) while C₁₄TAB cannot. We present a system whose (a) foams can be destroyed on demand, (b) surfactant loses its amphiphilicity, and (c) foaming solution can be reused. There are two novel contributions in the present study: (1) we compare the properties of a switchable surfactant with its non-switchable counterpart. In doing so, we clearly differentiate between the effect of the gas (CO₂ vs. N₂) and the effect of the switching (ON vs. OFF). (2) We used all possible combinations of pre-sparging (either with CO₂

or N₂) and foaming (either with CO₂ or N₂). In doing so, we can clearly distinguish between the time scales for foam generation and foam decay on the one hand and the time scale for switching on the other.

MATERIALS AND METHODS

Chemicals

CO₂ (purity 99.99%) and N₂ (purity 99.99%) were purchased from *SOL Deutschland GmbH* and used as received. N,N-dimethyltetradecylamine (C₁₄DMA) was purchased from *BLD Pharm* (purity 99.7%). Tetradecyltrimethylammonium bromide (C₁₄TAB) was purchased from *Sigma Aldrich* (purity ≥99%). Both surfactants were used as received. All the glassware was cleaned before use with deconex[®] UNIVERSAL 11 from *Borer Chemie* and rinsed several times with distilled water to remove all possible impurities. The solutions were prepared with double distilled water at room temperature (22 ± 1°C).

Solubility of C₁₄DMA

The neutral form of C₁₄DMA is an insoluble, low density, organic liquid which floats on top of water. When CO₂ is added to the solution via a dispersion tube, the amine becomes protonated transforming the molecule into a cationic surfactant: the solution becomes clear as the surfactant is completely soluble in water. The clear solution can now be foamed with CO₂. When CO₂ is removed from the solution by sparging N₂ into the solution, the solution becomes cloudy again indicating that the molecule reverts back to its insoluble neutral form.

The solubility limit of neutral C₁₄DMA was determined using a similar method as the one reported by Su et al., 2014. ¹H NMR spectroscopy was used to measure the solubility limit of the neutral form of C₁₄DMA in D₂O. D₁₄DMA (0.048 g, 0.20 mmol) was dissolved in 3 ml of D₂O and stirred for 30 min in a sample vial. The mixture was then allowed to stand for 30 min. A 200 μl sample was taken and combined with 10 μl of DMF as a standard in an NMR tube. The NMR tube was topped up with D₂O (0.6 ml) and a ¹H NMR spectra was measured. The ratio of C₁₄DMA to DMF was used to determine the solubility limit of C₁₄DMA (repeated three times). The maximum concentration of C₁₄DMA in D₂O is as low as 3.3 × 10⁻¹¹ M.

Surface tension measurements

Surface tensions of the aqueous surfactant solutions were determined as a function of the surfactant concentration under air for C₁₄TAB and under CO₂ for

C₁₄DMA using the profile analysis tensiometer (PAT1) (SINTERFACE Technologies, Germany). Before measuring the surface tensions, the capillary was rinsed several times with double distilled water. For C₁₄DMA, the concentrated surfactant solution was sparged with CO₂ via a P2 (41–100 μm pore diameter) dispersion tube for 20 min to convert C₁₄DMA into a surfactant. The glass measuring cell was rinsed with double distilled water and 5 ml of the surfactant solution to be investigated; 15 ml of surfactant solution was placed in the glass measuring cell to be measured. The capillary was then positioned in the measuring chamber. The desired gas was sparged into the air space of the chamber through a hole at the top of the measuring cell and sealed. A buoyant bubble filled with either air for C₁₄TAB or CO₂ for C₁₄DMA was pushed through a steel capillary of 2 mm in diameter that is inserted into the surfactant solution (V = 15 ml). During measurements, the drop volume was kept constant at all surfactant concentrations to make sure that the bubble remained an oval shape. Measurements were taken at 22 ± 1°C until a constant surface tension value was reached. The obtained surface tension value was the average of the last five values of the plateau.

Foam measurements

The FoamScan from Teclis (TECLIS, France) was used to determine the foam properties of the aqueous surfactant solutions. The FoamScan uses image analysis and conductivity measurements to monitor foamability, foam stability, liquid fraction, bubble size, and bubble size distribution. The bubble size and bubble size distribution were analyzed using the cell size analysis (CSA) function. For a detailed description of the FoamScan and CSA method, the reader is referred to (Boos et al., 2013; Carey & Stubenrauch, 2009; Carey & Stubenrauch, 2010). The aqueous surfactant solutions were used at a concentration 10 times the *cmc* to account for any depletion that occurs during foaming (Boos et al., 2012). The aqueous C₁₄DMA solution was sparged with either CO₂ or N₂ via a P2 (41–100 μm pore diameter) dispersion tube for 20 min before addition to the FoamScan. A constant foam volume V_{end} = 120 ml is generated by sparging either N₂ or CO₂ into a liquid volume of V_s = 60 ml via a porous P2 (41–100 μm pore diameter) glass disc at a flow rate of Q = 100 ml min⁻¹. Each surfactant solution was measured three times to demonstrate reproducibility. Measurements were performed at 22 ± 1°C.

Conductivity measurements

The conductivity of the aqueous surfactant solutions was measured at 22 ± 1°C using a conductivity meter

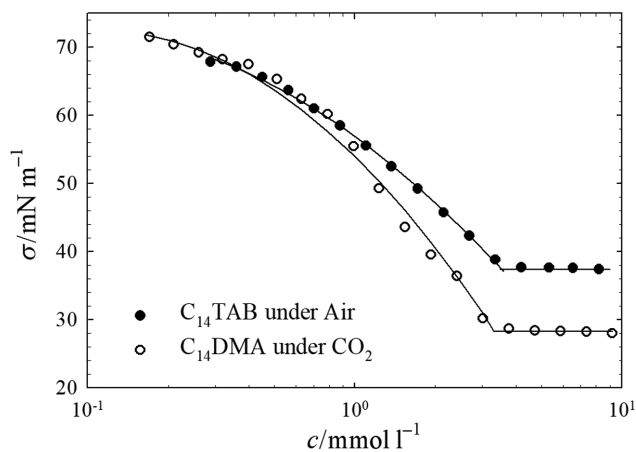


FIGURE 1 Surface tension of aqueous solutions of C_{14}DMA under CO_2 and C_{14}TAB under air as a function of the concentration at $22 \pm 1^\circ\text{C}$. The curves are fitted using second order polynomials

(inolab WTW series cond 720). CO_2 gas was first bubbled through the solution via a P2 ($41\text{--}100\ \mu\text{m}$ pore diameter) dispersion tube at $50 \pm 5\ \text{ml min}^{-1}$ until the conductivity no longer changed. Subsequently N_2 was bubbled through the solution at $50 \pm 5\ \text{ml min}^{-1}$ until the conductivity no longer changed. The gas flow was maintained using a mass flow controller GFC17 by Analyt. The CO_2 and N_2 treatments were carried out two more times for a total of three cycles.

RESULTS AND DISCUSSION

Before addressing the gas switchability of the surfactant N,N -dimethyltetradecylamine, C_{14}DMA , we need to identify a non-switchable counterpart for the sake of comparison and to look at the influence of the chosen gas on foam stability in general.

Surface properties

In order to distinguish between the effect of surfactant switching and the choice of gas on foam stability, a non-switchable counterpart needed to be found. The counterpart should have a similar surface activity as our ON form. Looking at Scheme 2, one sees that we need a cationic surfactant with a C_{14} -tail and an amine-based head group. From a structural point of view tetradecyltrimethylammonium bromide (C_{14}TAB) should be an appropriate non-switchable counterpart. In order to check this, we measured the surface tensions of C_{14}DMA in its ON form, that is, under CO_2 , as a function of the surfactant concentration and compared them with the surface tensions of C_{14}TAB . The results are shown on Figure 1 and Table 1.

The data shown in Figure 1 and Table 1 reveal that C_{14}DMA behaves like a “normal” surfactant under CO_2

with a critical micelle concentration of $\text{cmc} = 2.9\ \text{mM}$ and a plateau surface tension of $\sigma_{\text{cmc}} = 28.3\ \text{mN m}^{-1}$. These values are in line with the results of Binks who obtained $\text{cmc} = 2\text{--}3\ \text{mM}$ and $\sigma_{\text{cmc}} = 28\text{--}30\ \text{mN m}^{-1}$ for C_{14}DMA under CO_2 (Binks, 2021). We recall that under air (i.e., under N_2) C_{14}DMA is an insoluble oil with no surface-activity.

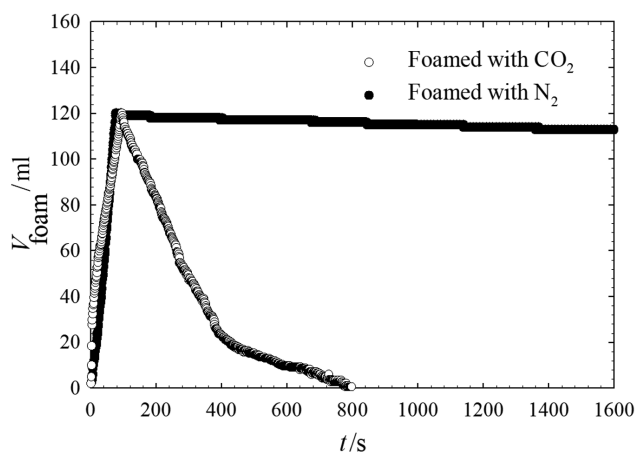
Comparing the surface tension curve of C_{14}DMA under CO_2 with that of C_{14}TAB under air one sees that the cmc -values are very similar. What is different are the values for the plateau surface tension σ_{cmc} , the maximum surface concentration Γ_{max} , and the minimum head group area A_{min} . The lower σ_{cmc} -value of C_{14}DMA indicates that C_{14}DMA is more densely packed in the surfactant monolayer than C_{14}TAB which is also reflected in Γ_{max} and A_{min} . The reason for this observation is the different sizes of the head groups: the ON form of C_{14}DMA has two methyl groups and one hydrogen attached to the nitrogen, while in the head group of C_{14}TAB three methyl groups are attached to the nitrogen. Nevertheless, since the surface-activity is mainly reflected in the cmc values (which are very close) it is appropriate to consider C_{14}TAB a non-switchable counterpart for C_{14}DMA .

Influence of gas choice on foam stability

In order to study the influence of N_2 and CO_2 , respectively, on foam stability, we generated foams with aqueous solutions of the non-switchable surfactant C_{14}TAB at a concentration of $10\ \text{cmc}$ and measured their time evolution. Looking at Figure 2, one sees that the foamability, that is, the time it takes to generate $120\ \text{ml}$ of foam, is not affected by the type of gas. However, the decay of the foam volume is very different; while the volume of the foam generated with N_2 hardly changes over $1600\ \text{s}$, the foam generated with CO_2 completely collapses after $800\ \text{s}$. The reason for this difference is coarsening, that is, the growth of larger bubbles at the expense of smaller bubbles due to the larger Laplace pressure of the smaller bubbles (Saint-Jalmes, 2006; Stevenson, 2010). Coarsening happens in any polydisperse foam but since it depends (i) on the gas solubility in the aqueous surfactant solution and (ii) on the diffusivity of the gas through the liquid foam films the type of gas matters. While the gas diffusion coefficients of different gases in water are of the same order of magnitude ($D_{\text{gas}} \sim \times 10^{-9}\ \text{m}^2\ \text{s}^{-1}$), their solubility in water differs greatly (Yu & Kanj, 2022). Important for our study is the fact that the solubility of CO_2 in water is nearly 100 times larger than that of N_2 ; the solubility of CO_2 in water at 20°C is $1.702\ \text{g L}^{-1}$, while the solubility of N_2 in water at 20°C is $0.0183\ \text{g L}^{-1}$ (Lide, 2001). Farajzadeh et al., 2014 studied the effect of the gas solubility on foam stability by monitoring the foam half-life (the time after which 50% of the foam

TABLE 1 Critical micelle concentration (cmc), plateau surface tension (σ_{cmc}), maximum surface concentration (Γ_{max}), and minimum head group area (A_{min}) for C₁₄DMA under CO₂ and for C₁₄TAB under air

Surfactant	cmc/mM	$\sigma_{\text{cmc}}/\text{mN m}^{-1}$	$\Gamma_{\text{max}}/10^{-6} \text{ mol m}^{-2}$	$A_{\text{min}}/\text{\AA}^2$
C ₁₄ DMA under CO ₂	2.9	28.3	5.0 ± 0.6	33 ± 2
C ₁₄ DMA under CO ₂ (Binks, 2021)	2–3	28–30		
C ₁₄ TAB under air	3.3	38.7	3.7 ± 0.3	45 ± 3
C ₁₄ TAB under air (Bergeron, 1997)	3.5	39.0	3.5	46

**FIGURE 2** Time evolution of the foam volume for aqueous foams stabilized by C₁₄TAB using either CO₂ or N₂ as the dispersed gas at 22 ± 1°C. The FoamScan was set to reach a maximum foam volume of 120 ml with a flow rate of 100 ml min⁻¹. A surfactant concentration of $c = 33 \text{ mM}$ ($\cong 10 \text{ cmc}$) was used

volume are decayed). They found that the foam stability decreases with increasing gas solubility, that is, foams stabilized with N₂ are the most stable ones, while foams generated with CO₂ are the least stable ones (it holds for the foam stability: N₂ > CH₄ > He > CO₂ and for the water solubility: N₂ < CH₄ < He < CO₂) (Farajzadeh et al., 2014). Our finding is thus perfectly in line with what one expects, namely a much higher stability of foams generated with N₂ compared with those generated with CO₂. We need this piece of information in order to distinguish between the effect of the gas and the effect of the surfactant switching on foam stability as will be discussed in the next section.

Foam properties and switching behavior

Firstly, we compare the initial structures of foams stabilized with C₁₄TAB and the ON form of C₁₄DMA, respectively, foamed with either N₂ or CO₂. To generate the ON form of C₁₄DMA, the aqueous solution was sparged with CO₂ for 20 min to fully protonate the amine (this solution is labeled Cp-C₁₄DMA in the following). The solutions were then added to the foam column and the FoamScan was set to reach a maximum foam volume of 120 ml with gas being sparged through the

solution at 100 ml min⁻¹. Pictures of the foam structure were captured at $t = 0$ which corresponds to the point at which 120 ml of foam was generated and the gas input was stopped. The surfactant concentration was always 10 cmc to account for depletion during foaming (Boos et al., 2012). The initial mean radii $\langle r \rangle$ of the foam bubbles, the initial liquid fractions ε , and the polydispersity indices PI are shown in Figure 3 and Table 2.

Looking at Figure 3 and Table 2, one sees the following trends: (a) The bubbles of foams generated with N₂ are larger than those of foams generated with CO₂, the reason for which is unclear. (b) If one pre-sparges the C₁₄DMA solution with N₂ (this solution is labeled Np-C₁₄DMA in the following) and subsequently tries to foam it with CO₂, surfactant needs to be generated in the first place. We will see further below that the complete conversion to the ON form takes more time than foam formation. In other words, a full conversion of C₁₄DMA is not required for foam formation. As a consequence, the N₂ pre-sparged solution contains less surfactant than the solution that was pre-sparged with CO₂ which leads to larger bubbles (smaller surface area). (c) The polydispersity indices of foams generated with N₂ are smaller than those of foams generated with CO₂, which can be explained by the quick coarsening that already takes place during foam generation. (d) For the initial liquid fractions, no trend can be observed. In a nutshell, the initial foam properties are very similar as were the surface properties. Let us now look at the time evolution of the foam volume.

Foamed with N₂

Looking at Figure 4 (top) one sees that the Np-C₁₄DMA solution is indeed incapable of producing any foam. The C₁₄DMA is completely switched OFF, that is, it is a water insoluble oil with which no foaming is possible. Opposed to this, the Cp-C₁₄DMA solution forms 120 ml of foam in about 100 s as does the C₁₄TAB solution. In other words, the foamability of the two solutions is equal (as were the initial foam and the surface properties). The time evolution of the foam volume, however, is different. While the volume of the foam stabilized with C₁₄TAB hardly changes over 1600 s, the volume of the foam stabilized with the ON form of C₁₄DMA decreases by about 70% in the same period of time. More

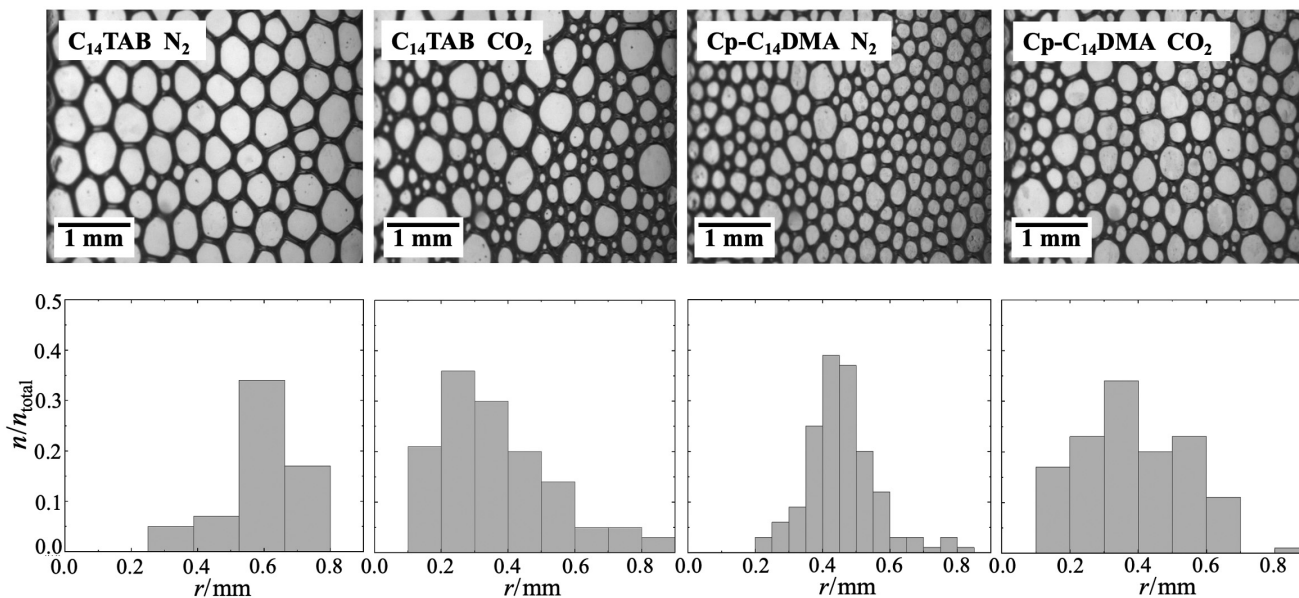


FIGURE 3 Foam bubble patterns (top) and bubble size distribution (bottom) for aqueous foams stabilized by either $C_{14}TAB$ or $Cp-C_{14}DMA$ using either CO_2 or N_2 as the dispersed gas. Photographs were taken immediately after the maximum foam volume of 120 ml was reached and the gas input was stopped

TABLE 2 Mean radii ($\langle r \rangle$) of foam bubbles, total number of foam bubbles (n_{total}), initial liquid fraction (ϵ), and polydispersity index (PI) for aqueous foams stabilized by either $C_{14}TAB$ or $Cp-C_{14}DMA$ using either CO_2 or N_2 as the dispersed gas

Surfactant	$\langle r \rangle / \text{mm}$	n_{total}	ϵ	PI
$C_{14}TAB$ foamed with N_2	0.59 ± 0.01	65	0.04	0.19
$C_{14}TAB$ foamed with CO_2	0.36 ± 0.02	134	0.11	0.46
$Cp-C_{14}DMA$ Foamed with N_2	0.46 ± 0.01	162	0.07	0.22
$Cp-C_{14}DMA$ Foamed with CO_2	0.38 ± 0.02	129	0.08	0.40
$Np-C_{14}DMA$ Foamed with CO_2	0.76 ± 0.02	56	0.06	0.47

Note: Measurements were made at $t = 0$ which corresponds to the time at which 120 ml of foam was formed and the gas supply was stopped.

precisely, the foam volume starts decreasing after an “onset time” of about 600 s (10 min). The moment the $Cp-C_{14}DMA$ solution is sparged with N_2 the ON form of $C_{14}DMA$ starts turning OFF. According to the foam measurements, it takes about 10 min until enough cationic $C_{14}DMA$ is deactivated to visibly affect the foam properties. Obviously, a full conversion of the surface-active cationic $C_{14}DMA$ to the surface-inactive neutral $C_{14}DMA$ is not required for foam destabilization: once a certain conversion rate is reached, the foam starts decaying continuously. It is this decay which can be assigned to the switching capability of $C_{14}DMA$ and which distinguishes $C_{14}DMA$ from the non-switchable $C_{14}TAB$.

Foamed with CO_2

Looking at Figure 4 (bottom) one sees that foams stabilized by the $Cp-C_{14}DMA$ and the $C_{14}TAB$ solution, respectively, behave the same in terms of foamability

and foam stability. In both cases it takes about 100 s to generate 120 ml of foam which then decays quickly due to fast coarsening the foams are completely destroyed after 800 s. As already discussed in connection to the surface and the initial foam properties, the $V(t)$ -curves in Figure 4 (bottom) show again that the switchable $C_{14}DMA$ molecule behaves exactly like its non-switchable counterpart if it is switched ON. An additional piece of information is provided by the $V(t)$ -curve of the foam stabilized by the $Np-C_{14}DMA$ solution. Here we start with $C_{14}DMA$ in its OFF form, which is subsequently switched ON during sparging the solution with CO_2 . After ~ 100 s enough molecules are switched on to stabilize foam in general and after ~ 400 s enough molecules are switched on to stabilize 120 ml of foam in particular. Note that the foamability is lower compared with the foams stabilized by the $Cp-C_{14}DMA$ solution (~ 250 s compared with ~ 100 s) since foaming and production of the ON form happen simultaneously—foam can only be stabilized if enough surfactant has formed. The conversion obviously

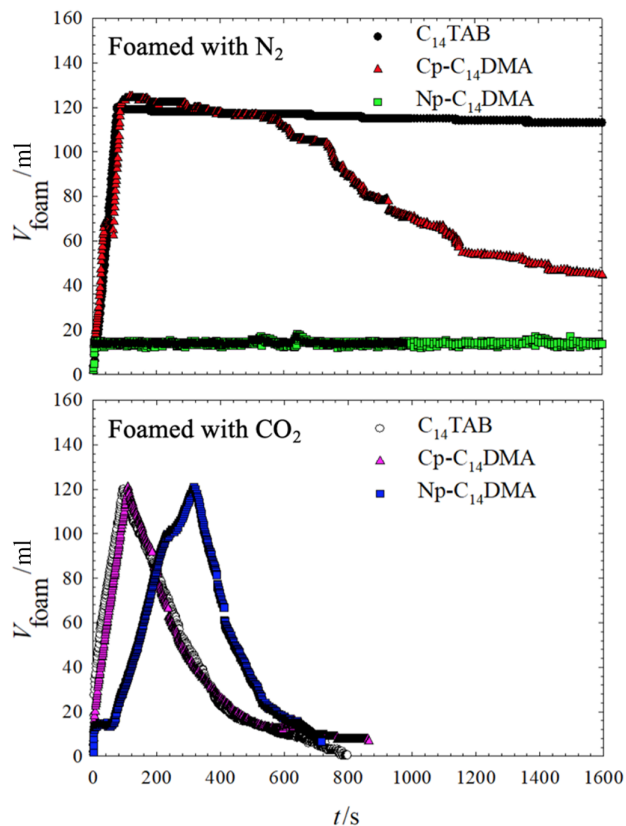


FIGURE 4 Time evolution of the foam volume for aqueous foams stabilized by either $C_{14}TAB$, $Cp-C_{14}DMA$ or $Np-C_{14}DMA$ using either N_2 (top) or CO_2 (bottom) as the dispersed gas at $22 \pm 1^\circ C$. The FoamScan was set to reach a maximum foam volume of 120 ml with a flow rate of 100 ml min^{-1} . A surfactant concentration of $c = 33 \text{ mM}$ and $c = 29 \text{ mM}$ (10 cmc) was used for $C_{14}TAB$ and $C_{14}DMA$, respectively

happens on the time scale of foam formation. We will see further below that after 400 s only a portion of the $C_{14}DMA$ is switched ON. As was the case for foams generated with N_2 , a full conversion of the surface-inactive neutral $C_{14}DMA$ to the surface-active cationic $C_{14}DMA$ is not required for foam stabilization. In conclusion, we showed that CO_2 pre-sparged $C_{14}DMA$ solutions and $C_{14}TAB$ solutions have the same foaming properties if the foams are generated with CO_2 . However, if the foams are generated with N_2 one clearly sees a difference: because $C_{14}DMA$ is continuously switched OFF in the presence of N_2 , the foam destabilizes faster than the foam stabilized by the non-switchable counterpart $C_{14}TAB$. Both foam stabilization and destabilization are continuous processes which occur in parallel with the continuous switching.

We will finish this chapter by looking at the reversibility and repeatability of switching between the neutral and the protonated form of $C_{14}DMA$. For that purpose, we measured the conductivity of a 29 mM (10 cmc) aqueous $C_{14}DMA$ solution. CO_2 and N_2 were sparged through the solution over three cycles at $22 \pm 1^\circ C$. As can be seen in Figure 5, bubbling of CO_2 increases the

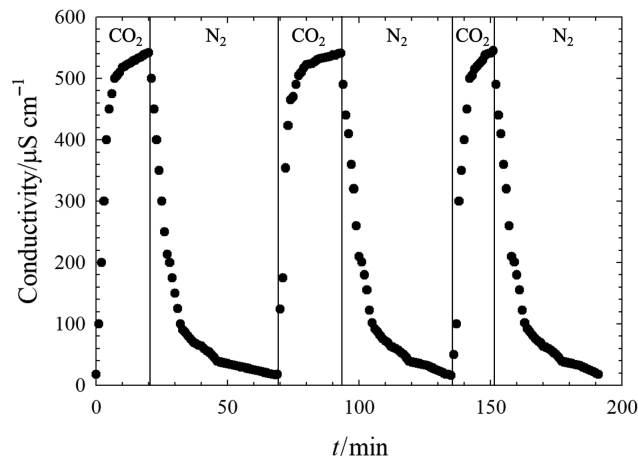


FIGURE 5 Conductivity of a 29 mM (10 cmc) $C_{14}DMA$ solution as function of time during alternating sparging of CO_2 and N_2 through the solution at $50 \pm 5 \text{ ml min}^{-1}$ and $22 \pm 1^\circ C$

conductivity of the solution from 18 to $542 \mu S \text{ cm}^{-1}$ in 20 min due to the conversion of the neutral $C_{14}DMA$ to the cationic $C_{14}DMA$ surfactant. Subsequently bubbling N_2 through the solution one sees that the conductivity decreases down to its original value after 50 min. The same pattern occurred in the next two cycles, which shows that $C_{14}DMA$ can be switched from neutral to ionic and back again by the addition and removal of CO_2 . Comparing the conductivity with the foam measurements one sees that there are two different time scales. As seen in Figure 5, it takes roughly 20 min of CO_2 sparging to convert the neutral $C_{14}DMA$ to the ON form and about 50 min to convert the cationic surfactant to the OFF form. However, it had only taken ~ 5 min of CO_2 sparging to generate a 120 ml foam from the $Np-C_{14}DMA$ solution (Figure 4, bottom) and ~ 10 min to destabilize the foam in the presence of N_2 (Figure 4, top). Thus, one has to distinguish between (a) the time it takes to completely convert $C_{14}DMA$ from the OFF to the ON form and vice versa and (b) the time it takes to generate or destabilize a foam. Obviously, foams can be stabilized with a mixture of the ON and the OFF form $C_{14}DMA$. Note that the flow rates for foaming (100 ml min^{-1}) and for the conductivity measurements ($50 \pm 5 \text{ ml min}^{-1}$) differ only by a factor of two, while the mentioned time scales differ by a factor of ~ 5 , that is, the different time scales are not caused by the different flow rates but by the fact that for foaming/defoaming only parts of $C_{14}DMA$ must be activated/deactivated. In future studies we will quantify the lowest amount of conversion required for foam stabilization/destabilization.

Conclusions and outlook

We showed that the CO_2 -switchable compound N, N-dimethyltetradecylamine ($C_{14}DMA$) stabilizes foams if its head group is protonated, that is, if the surface

activity is switched on. The resulting cationic surfactant has properties similar to those of its non-switchable counterpart tetradecyltrimethylammonium bromide (C_{14} TAB) with one exception: it can be switched OFF on demand with N_2 . This is advantageous in industrial applications where foam is desired for one part of the process and undesired for another. For example, in mining the foam can be generated with CO_2 in the rocks and it is destroyed again by simply getting into contact with air after leaving the rocks. The water insolubility of the neutral C_{14} DMA can also be looked at as an advantage. Once foam is no longer desired, N_2 can be sparged into the foam causing phase separation of the neutral amine and water. The amine can be removed from the water by simple liquid separation thus eliminating the need for energy-intensive methods like distillation to collect and reuse the surfactant. We thus have succeeded in identifying a system whose (a) foams can be destroyed on demand, (b) surfactant simultaneously loses its amphiphilicity, and (c) foaming solution can be reused.

In some applications, however, it may be important to maintain a N_2 or air foam for an extended period and yet retain the ability to collapse the foam upon demand. C_{14} DMA is incapable of meeting that need because it switches OFF in an N_2 -generated foam, giving the foam an artificially short lifetime. CO_2 -switchable surfactants with the reverse behavior (ON under N_2 or air, OFF under CO_2) would be better for such applications; the N_2 or air foams would be as stable as those with non-switchable surfactants but would be destabilized upon exposure to CO_2 . Surfactants with a CO_2 -switchable amine group in the tail, rather than the head group, exhibit this reverse behavior. Their ability to stabilize foams will be the subject of a separate publication.

AUTHOR CONTRIBUTIONS

Hailey Poole conceptualization of the study, carried out the research and wrote the first draft of the manuscript, Philip G. Jessop conceptualization of the study, writing-review and editing of the manuscript, supervision of study, Cosima Stubenrauch conceptualization of the study, writing-review and editing of the manuscript, supervision of study. All authors contributed to and approved the final draft of the manuscript.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

ETHICS STATEMENT

This research falls outside of human or animal studies and institutional ethical approval was not required.

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SUPPORTING INFORMATION

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