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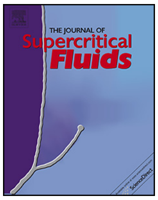

Effect of surfactant headgroup on low-fluorine-content CO_2-philic hybrid surfactants

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ABSTRACT

The article addresses the role of surfactant headgroup structure on hybrid surfactant performance for water-in-CO_2 (w/c) microemulsion stabilization. The synthetic procedure, aqueous properties, and phase behaviour of a new hybrid sulfoglutarate surfactant are described. The sulfoglutarate version has an extra methylene group incorporated into the hydrophilic headgroup. The related hydrocarbon (AOT14 and AOT14GLU) and fluorocarbon (di-CF2 and di-CF2GLU) surfactants were used to form w/c microemulsions. For these two groups, the aqueous properties and w/c phase stability of both sulfoglutarates and sulfosuccinates were found to be similar. The newly synthesized hybrid CF2/AOT14GLU (sodium (*4H,4H,5H,5H,5H*-pentafluoropentyl-2,2-dimethyl-1-propyl)-2-sulfoglutarate) proved to be more efficient than the normal sulfosuccinate, hybrid CF2/AOT14 in terms of the aqueous behaviour and w/c phase stability. Hybrid CF2/AOT14GLU more effectively decreased the air-water surface tension by ~2 mN m^{-1} and lowering the cloud pressures on CO_2 by ~150 bar.

1. Introduction

Supercritical carbon dioxide (sc-CO_2) is considered a desirable solvent for green materials and chemical processing [1,2], so sc-CO_2 has been used for various applications [3,4] and interest still remains high today [5–8]. As such CO_2 is a nonpolar molecule with low dielectric constant and solubility parameter, which makes it unsuitable for dissolving polar and high-molecular-weight materials [9]. These weak solvent properties undoubtedly limit the practical applications of sc-CO_2. One effective approach to overcome these problems is to use CO_2-philic surfactants to stabilize microemulsion phases, for example, water-in-CO_2 (w/c) microemulsions. The formation of reverse micelles with water pools inside bulk CO_2 provides a microenvironment for materials which are otherwise sparingly soluble or insoluble in CO_2, whereas nonpolar materials are solubilized in the CO_2-continuous phase [10–12].

Fluorination is considered a key feature for generating CO_2-philic surfactants [13,14]. An investigation using several fluorinated analogues of the common anionic surfactant Aerosol-OT (AOT) shows that an increase in the level of surfactant chain fluorination leads to a decrease in the limiting air-water (a/w) aqueous surface tension (γ_{cmc}) and a decrease in the phase transition pressure of w/c microemulsions; w/c phase cloud pressure (P_{trans}) [15]. However, concerns have been raised because the use of long fluorocarbon chains represents an environmental threat. These issues have been addressed using low F-content hybrid surfactants, where separate fluorocarbon and hydrocarbon chains are chemically bonded to the same hydrophilic headgroup to generating more environmentally-responsible CO_2-philic surfactants [16,17].

The role of the surfactant chemical structure in w/c phase stability has been a central issue in CO_2 studies and research has been conducted to determine how changes in surfactant molecular structure can affect physicochemical properties of surfactant aqueous solutions and w/c phase stability [13,18–21]. A traditional concept of the molecular packing parameter (p) [22] has been widely invoked to explain the correlation between the molecular structure and the surfactant self-assembly. This geometric parameter is defined as $p = v_0/a_e l_0$ and includes the contributions of the

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volume (v_0) and length (l_0) of the surfactant tail and the interfacial area each surfactant molecule occupies (a_e) (which is referred to as the headgroup area in most cases).

Studies using double chain anionic surfactants have been devoted to the effect of structural modifications of the surfactant chains with limited surface tension ability, w/c phase stability, and surfactant solubilizing power [15,23–27]. Branching, methylation, and fluorination of the chain tips have been shown to induce more favorable tail-CO_2 interactions which improve CO_2 compatibility [28,29]. A study on hybrid surfactants has shown that for a constant headgroup type and fluorocarbon chain structure the surfactant performance is notably affected by modification of the hydrocarbon CO_2-philic chain structure. Trends in the concentration at which the surfactant molecules starts to aggregate into micelles i.e. critical micelle concentration (cmc), the area occupied per surfactant molecule at the cmc (A_{cmc}), and w/c phase stability were found to link closely with the degree of chain branching, and this can be quantified using an empirical branching factor [30]. A convenient way to rank the effectiveness of surfactants in w/c systems is using the molar solubilization ratio w = [water]/[surfactant]: under equivalent P and T conditions, hence, the higher w the more effective the surfactant. The hydrophilic headgroup chemical structure has not been systemically studied, mainly because of a lack of suitable compounds; hence, most studies focused on the effects of counterions and headgroup polarity [31–34]. The most relevant work [15,23,35] investigated glutarate analogues of the normal sulfosuccinate surfactant.

Sulfoglutarate surfactants (denoted as GLU) were obtained using fluorinated AOT-analogues, for example sodium bis (1*H*, 1*H*, 5*H*-octafluoropentyl)-2-sulfosuccinate (di-HCF4; $\gamma_{cmc} = 26.8\ mN\ m^{-1}$, $P_{trans} = 193$ bar; $w = 10$ at 25 °C) and the related compound sodium bis (1*H*, 1*H*, 5*H*-octafluoropentyl)-2-sulfoglutaconate (di-HCF4GLU; $\gamma_{cmc} = 25.4\ mN\ m^{-1}$, $P_{trans} = 181$ bar; $w = 10$ at 25 °C) [15,23]. Changing sulfosuccinate headgroup for sulfoglutarate increases the hydrophobicity (cmc) and surface-tension-lowering ability, whereas only a subtle change on the A_{cmc} is observed. There is also a slight enhancement of the w/c phase stability with the sulfoglutarate surfactant. Another highly interesting observation with sulfoglutarate surfactants was reported by Sagisaka et al. [36–39] using two related compounds: sulfosuccinate $nFS(EO)_2$ and sulfoglutarate $nFG(EO)_2$ (n = 4, 6, 8). Visual observation and UV–vis measurements, with the probe dye methyl orange (MO) as a tracer, showed that sulfoglutarate attains higher solubilizing power for w/c microemulsions in CO_2 than the sulfosuccinates. Moreover, $4FG(EO)_2$ (sodium 1,5 bis [(1*H*, 1*H*, 2*H*, 2*H*-perfluorohexyl)oxy]-1,5-dioxopentane-2-sulfonate) has the highest solubilizing power w reported to date ($w \sim 80$), which is a significant improvement over other known CO_2-philic surfactants.

Using the glutarate analogues of AOT and di-C6SS, which are denoted as AOTGLU and di-C6GLU, respectively, Nave et al. [35] showed that sulfoglutarate and sulfosuccinate surfactants have notably similar aqueous properties, e.g., critical micelle concentration, cmc, γ_{cmc} and microemulsion phase stability. Sagisaka et al. [29] also reported the effect of an additional $-CH_2$- spacer on surfactant solution physicochemical properties with two series of highly branched AOT analogue surfactants: di-BC_n*SS* (sulfosuccinate type) and di-BC_n*SG* (sulfoglutarate type). In most cases, for hydrocarbon surfactants a modification of the hydrophilic headgroup exerts a weaker effect on the limiting surface tension than for analogous fluorinated surfactants.

Following on from the previous work, this paper aims to investigate the effect of hydrophilic headgroup modification on the performance of novel hybrid sulfoglutarate surfactant for w/c microemulsions stabilization. The glutarate analogue of the hybrid sulfosuccinate surfactant was synthesized, and the performance was investigated. To minimize the fluorination, in this work the fluorocarbon chain of the hybrid surfactant was fixed using the low-fluorine-content di-CF2 tail [40], whereas the hydrocarbon chain is an AOT14 tail (Table 1), which is the di-chain analogue of the CO_2-soluble tri-chain TC14 (sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulfonate) surfactant [41]. The performance of the related hydrocarbon and fluorinated surfactants are included. The chemical structures of hybrid, hydrocarbon, and fluorinated sulfoglutarate surfactants, which are denoted as hybrid CF2/AOT14GLU, AOT14GLU, and di-CF2GLU, respectively, and the normal sulfosuccinate, are provided in Table 1. Sulfosuccinates and sulfoglutarates differ in only the headgroup structures: with the addition of an extra$-CH_2$- spacer on the hydrophilic part, so that sulfoglutarate surfactants now have a symmetrical headgroup with respect to the $-SO_3Na$ function. This study provides new information on how the hydrophilic-headgroup structure influences surfactant performance in w/c systems, particularly regarding hybrid surfactants, and fuels research into low-fluorine-content CO_2-philic surfactants.

2. Experimental section

2.1. Materials

Synthesis of sulfosuccinate surfactants was previously reported [40,42]. Sulfoglutarate surfactants were prepared using the same alcohol precursors as used for sulfosuccinate surfactants. The fluorinated and hydrocarbon sulfoglutarate surfactants were synthesized using a Dean and Stark apparatus [39]. Esterification step was included to obtain the hybrid sulfoglutarate surfactant. Further information on the hybrid-sulfoglutarate-surfactant synthesis can be found in Section 2.2. Neopentyl alcohol 98% (Acros Organics) and 4*H*, 4*H*, 5*H*, 5*H*, 5*H*-pentafluoropentanol (Apollo Scientific) were used without further purification. Dimethyl glutaconate ≥97% (Sigma Aldrich) was used without further treatment. Maleic anyhidride (99%) and sodium hydrogen sulfide (98%) were obtained from Friendemann Schmidt. *p*-toluene sulfonic acid monohydrate (98%) was obtained from Merck and used as received. Distilled water (Otsuka Pharmaceutical, injection grade, pH = 6.5) and CO_2 (Tomoe Shokai, 99.99%) were used as received.

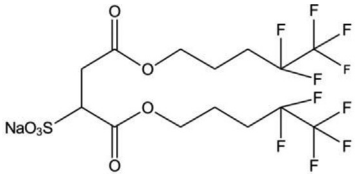
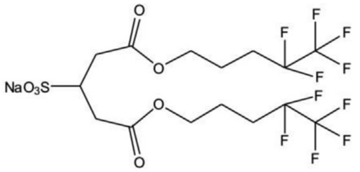
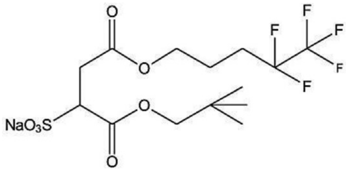
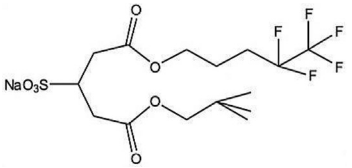
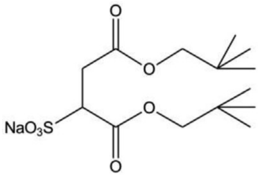
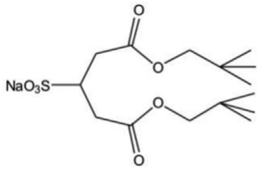
2.2. Surfactant synthesis

2.2.1. Synthesis of hybrid CF2/AOT14GLU diester

A mixture of dimethyl glutaconate (1.0 eq), 4*H*,4*H*,5*H*,5*H*,5*H*—pentafluoropentanol (1.0 eq), and *p*-toluene sulfonic acid monohydrate (0.1 eq) in toluene (100 ml/5 g dimethyl glutaconate) was reacted overnight under reflux to produce the fluorinated monoester. During the transesterification reaction, methanol was azeotropically liberated to shift the reaction equilibrium and used as an indicator for the reaction completion. After the reaction was considered complete, the CF2-monoester was washed with warm water (70 °C). The fluorinated monoester was obtained as yellow transparent liquid after rotary evaporation of the solvent.

To produce the hybrid CF2/AOT14GLU diester, CF2-monoester (1.0 eq) and 2,2-dimethyl propanol (1.0 eq) were dissolved in toluene (10 ml/g monoester) in the presence of *p*-toluene sulfonic monohydrate (0.1 eq). The reaction was performed overnight to remove methanol as a result of the transesterification reaction. Then, the hybrid CF2/AOT14GLU diester was cooled to 70 °C and repeatedly washed with warm water to remove the unreacted *p*-toluene sulfonic monohydrate. The brown crude diester was obtained by rotary evaporation.

Table 1
Chemical structures of surfactants used in this study.

Surfactant	Structure	Chemical Name
di-CF2		Sodium bis (4*H*,4*H*,5*H*,5*H*,5*H*-pentafluoropentyl)-2-sulfosuccinate
di-CF2GLU		Sodium bis (4*H*,4*H*,5*H*,5*H*,5*H*-pentafluoropentyl)-2-sulfoglutarate
Hybrid CF2/AOT14		Sodium (4*H*,4*H*,5*H*,5*H*,5*H*-pentafluoropentyl-2,2-dimethyl-1-propyl)-2-sulfosuccinate
Hybrid CF2/AOT14GLU		Sodium (4*H*,4*H*,5*H*,5*H*,5*H*-pentafluoropentyl-2,2-dimethyl-1-propyl)-2-sulfoglutarate
AOT14		Sodium bis (2,2-dimethyl-1-propyl)-2-sulfosuccinate
AOT14GLU		Sodium bis (2,2-dimethyl-1-propyl)-2-sulfoglutarate

2.2.2. *Synthesis of the hybrid CF2/AOT14GLU surfactant*

The crude hybrid CF2/AOT14GLU diester (1.0 eq) was dissolved in ethanol (100 ml), and water was added to the mixture until saturation. After sodium hydrogen sulfite (4.0 eq) was added, the reaction mixture was refluxed for 72 h. The reaction was monitored using thin layer chromatography (TLC) eluted with ethyl acetate and considered complete when the diester TLC spot (Rf ~ 0.9) disappeared. The product formation was indicated by the appearance of the baseline surfactant spot (Rf ~ 0). The solvents were evaporated, and a white crude surfactant remained, which was left to dry overnight in an oven at 70 °C. Then, the crude surfactant was dissolved in dried acetone and centrifuged to remove any remaining inorganic impurity from the sulfonation step. The pure surfactant was obtained as a white yellowish powder after drying in an oven overnight at 60 °C (average yield = 40%).

Hybrid CF2/AOT14GLU

^{1}H NMR (500 MHz, $CDCl_3$, TMS), (δ_H/ppm): 0.88–0.97 (a, s, 9H), 1.86–1.99 (b, m, 2H), 2.08–2.19 (c, m, 2H), 2.56–2.72 (d, m, 2H), 2.98–3.11 (e, m, 2H), 3.70–3.82 (f, m, 4H), 4.08–4.22 (g, m, 1H). Elemental analysis: found C, 36.46; H, 5.17; S, 6.30. Calcd C, 38.80; H, 4.78; S, 6.90.

di-CF2GLU

^{1}H NMR (500 MHz, $(CD_3)_2CO$, TMS), (δ_H/ppm): 1.92–1.98 (a, m, 4H), 2.26–2.37 (b, m, 4H), 2.97 (c, s, 4H), 3.62–3.3.71 (d, m, 4H), 4.19–4.26 (e, m, 1H). Elemental analysis: found C, 32.77; H, 2.58; S, 6.17. Calcd C, 32.50; H, 3.09; S, 5.78.

AOT14GLU

^{1}H NMR (500 MHz, $(CD_3)_2CO$, TMS), (δ_H/ppm): 0.88–0.94 (a, t, 18H, J = 14.85 Hz), 2.66–2.70 (b, dd, 4H, J = 6.85, 16.6 Hz), 3.76–3.78 (c, d, 4H, J = 10.3 Hz), 3.80–3.82 (d, s, 1H). Elemental analysis: found C, 44.59; H, 7.12; S, 9.35. Calcd C, 48.12; H, 7.27; S, 8.56.

2.3. *Surface tension measurements*

Air-water (a/w) surface tensions were measured using a Wilhelmy tensiometer (CBVP-A3, Kyowa Interface Science), which was equipped with a platinum plate. All measurements were performed at 25 °C until the surface tension of the surfactant aqueous solu-

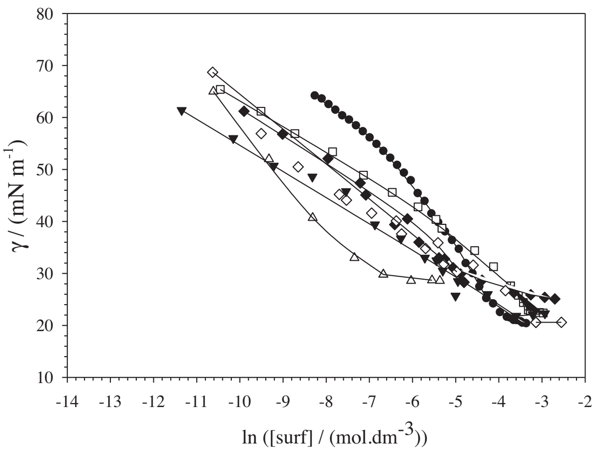


Fig. 1. Air-water surface tension (γ_{cmc}) vs. ln (concentration) of surfactant at 25 °C Quadratic lines were fitted to the pre-cmc data are shown. The symbols ●, □, ◊, ▼, △, respectively denote di-CF2, hybrid CF2/AOT14, AOT14GLU, hybrid CF2/AOT14GLU, di-CF2GLU and AOT14.

tions reached constant values (to avoid any dynamic relaxation effects). Detailed information of the experimental procedures and apparatus are described elsewhere [36,43]. The critical micelle concentrations (cmc) of each surfactant solution were obtained from the intersection of the graph of the surface tension (γ) versus ln of concentration (ln c).

2.4. High-pressure phase behaviour and UV–vis absorption measurement

The changes in phase stability of the surfactant/water/CO_2 mixtures were visually observed at constant composition with varying temperature and pressure. The measurements were performed at pressures up to 400 bar and controlled temperatures ranging over 35–75 °C. These experimental conditions were chosen because some surfactants may not exhibit considerable solubility in sc-CO_2, this approach is used to achieve surfactant dissolution. A similar procedure has also been used by other groups dealing with CO_2-philic surfactants [25,27,36,37]. To obtain comparable results, the surfactant concentration was fixed at 0.24 mol% (~0.05 mol dm^{-3}). Meanwhile, to examine the aqueous core formation in w/c microemulsion, UV–vis absorption spectroscopy measurement with the probe dye methyl orange (MO) solution was performed. The temperature, pressure, surfactant and MO concentration were fixed at 45 °C, 400 bar, 0.05 mol dm^{-3} and 0.1 wt% in water, respectively. Predetermined amounts of surfactants and CO_2 were loaded into a variable-volume high-pressure optical cell. Then, water or MO solution was added to the surfactant/CO_2 mixture until clear Winsor IV microemulsions became turbid macroemulsions. Further information about the experimental procedures and apparatus can be found elsewhere [37,44].

3. Results and discussion

3.1. Air-water (a/w) surface tension measurement

3.1.1. Critical micelle concentrations (cmcs)

Fig. 1 shows the aqueous surface tension data of sulfosuccinate and sulfoglutarate surfactants at 25 °C as a function of surfactant concentration. The aqueous properties of each surfactant, which were derived from the surface tension measurements, are shown in Table 2. Previously [23,29,35], with several glutarate analogues of fluorinated and hydrocarbon surfactants, it has been shown that the cmc decreases after the —CH_2 spacer is added to the surfactant hydrophilic headgroup. However, the decreasing cmc following hydrophilic-headgroup modification does not always follow this simple pattern, because methylene and methyl groups that are added to the surfactant do not contribute equally [45]. The individual cmc between sulfoglutarate and normal sulfosuccinate for the three surfactant classes show the trend of increasing cmc when the headgroup architecture was changed (see Table 2). It is postulated that micelle formation is a result of the balance in tail-water and headgroup-water interactions, although the tails favor aggregation the headgroup remains hydrated [22,46].

3.1.2. Limiting surface tension

One important function of the surfactant is the ability to decrease the air-water surface tension to the limiting value γ_{cmc}, and this value importantly represents the surfactant effectiveness and is a property of interest for the approximation of w/c microemulsions [15]. Notice that the γ_{cmc} values of each surfactant are essentially similar for all surfactants considered (see Table 2). The differences are highly likely within experimental uncertainties (±0.5 mN m^{-1}). Thus, the addition of the —CH_2 group on the hydrophilic part exerts much less effect than if it would be placed in the alkyl chain instead [34,47]. Table 2 shows that the extra —CH_2- content in the hydrophilic group does not increase the overall surfactant hydrophobicity. In contrast, a prior study that used a series of linear di-chain sulfosuccinates, di-C*n*SS (n = 4–8), showed that the cmc of surfactants reduced to approximately three fourths for each —CH_2 that was added to the surfactant chains [47]. In addition, the increase in total carbon number by adding —CH_2- is believed to contribute to the ability of a surfactant in reducing the air-water surface tension [34,47]. However, the obtained data show one unexpected finding for low-surface-energy materials: the hybrid CF2/AOT14GLU exhibits a notably low γ_{cmc} (down to 20.6 mN m^{-1}), which is even lower than the fully fluorinated surfactant di-CF2GLU ($\gamma_{cmc} = 21.8$ mN m^{-1}). A double fluorocarbon (FC)-tail surfactant usually has a greater surface-tension-lowering ability than a single FC-tail one of the same FC length, and the γ_{cmc} value of the hybrid CF2/AOT14GLU was expected to be between those of di-CF2GLU and AOT14GLU. It may be expected that the ability of the hybrid CF2/AOT14GLU to stabilize w/c microemulsions is enhanced because this surfactant also proves to be notably efficient in decreasing air-water surface tension.

3.1.3. Surfactant coverage at the a/w interface

An important parameter characterizing the surface packing of surfactant molecules is the effective area occupied per molecule at the cmc (A_{cmc}/Å^2). This value is obtained from the tensiometric analyses which can be found in detail at the supplementary material. The pre-cmc data were fitted to quadratic functions to generate adsorption isotherms using Gibbs equation (Eq. (1)); thus, the areas per headgroup at the cmc (A_{cmc}) were calculated. The prefactor m = 2 is responsible for the ratio 1:1 of dissociating ions for ionic surfactants.

$$\Gamma = -\frac{1}{mRT}\frac{d\gamma}{d\ln c} \tag{1}$$

$$A_{cmc} = \frac{1}{\Gamma N_A} \tag{2}$$

For all cases, the sulfoglutarate surfactants exhibit notably larger A_{cmc} than sulfosuccinates, which follows the similar observed trends for hydrocarbon and fluorinated sulfoglutarate surfactants [29,35,38]. Considering that these two surfactant classes differ only in headgroup architecture, the changes in A_{cmc} can be ascribed to the effect of adding an extra —CH_2- to the surfactant hydrophilic part. Because of the presence of the —CH_2- spacer in the surfactant headgroup, the glutarate surfactants have slightly larger headgroups [48]. Moreover, the double tails of the sulfoglutarate

Table 2
Properties of hybrid surfactants in water and CO_2[a].

Surfactant	Fluorine/wt%	cmc[b]/(mmol/dm^3)	γ_{cmc}[c]/(mN m^{-1})	A_{cmc}/Å^2	P_{trans}[d]/bar (±40 bar)
di-CF2[e]	35.16	19.0	22.4	65	219
di-CF2GLU	34.27	27.4	21.8	123	249
Hybrid CF2/AOT14[f]	21.09	46.8	22.5	102	383
Hybrid CF2/AOT14GLU	20.46	55.0	20.6	135	232
AOT14	0.0	2.39	28.6	100	Incompatible
AOT14GLU	0.0	8.18	28.3	115	Incompatible

[a] Parameters derived from surface tension measurements at 25 °C.
[b] Critical micelle concentration.
[c] Surface tension at cmc.
[d] P_{trans} is visual observation on surfactant solubility at $w = 10$, w/c, 55 °C.
[e] Data collected by Mohamed et al. [40].
[f] Data collected by Mohamed et al. [30].

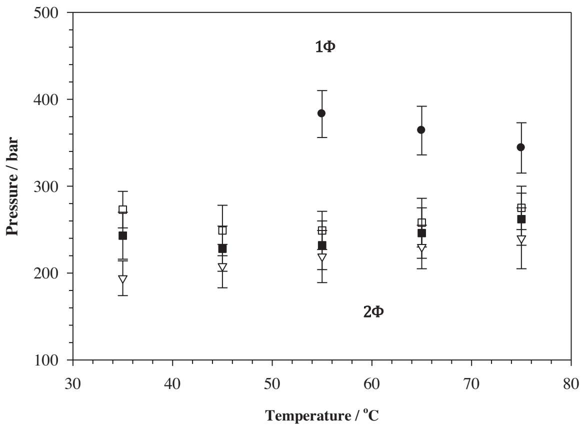


Fig. 2. Phase transition pressures for W/CO_2 microemulsions (1Φ) to W/CO_2 macroemulsions (2Φ) for surfactant/water/CO_2 mixtures with surfactant-to-CO_2 molar ratio = 0.0024 and water-to-surfactant molar ratio (w) = 10 at various temperatures. The symbols ●, □, ■, ▽, respectively denote hybrid CF2/AOT14, di-CF2GLU, hybrid CF2/AOT14GLU and di-CF2 surfactant. Surfactant molar concentration was in range between 0.03 and 0.06 mol dm^{-3}, for example 0.05 mol dm^{-3} at 45 °C and 400 bar as the inner volume of the cell was varied on changing the experimental pressure and temperature. The error bars represent the uncertainty of P_{trans} (±40 bar).

surfactant may be more open than those of the sulfosuccinates because of the extra linking spacer in the hydrophilic group [29,35,36]. These factors may cause the sulfoglutarate surfactants to occupy larger areas at the interface.

3.2. High-pressure phase behaviour

In CO_2 studies, high-pressure phase behaviour is necessary to seek the optimum conditions for stabilizing water-in-CO_2 microemulsions. Here, to readily compare the performance of all surfactants, a fixed surfactant concentration and water-to-surfactant molar ratio (w) were used. The value P_{trans} is the lowest pressure for a given composition and temperature at which the microemulsions remain single transparent one phase systems (1Φ); below P_{trans} phase separation occurs and the systems become turbid, indicating the formation of macroemulsions (2Φ). Hence, P_{trans} was used to evaluate the ability of the CO_2-philic surfactants to stabilize w/c microemulsions: the phase behaviour and P_{trans} values for the surfactants in this study are shown in Fig. 2 and Table 2, respectively.

Attempts to disperse water in dense CO_2 using both sulfosuccinate and sulfoglutarate versions of hydrocarbon surfactants (AOT14 and AOT14GLU) did not produce single transparent phases under the experimental conditions used here. Hence, the data for these two surfactants are not included in the phase diagram. Earlier studies on the identical system also reported the inability of the AOT14 surfactant to stabilize w/c microemulsions [42] despite the versatility of the parent AOT14; which is the tri-chain TC14 surfactant, in a wide range of solvents [41,49]. However, changing the hydrophilic headgroup into the larger sulfoglutarate was not sufficient to increase the tendency of the surfactants to stabilize w/c microemulsions. Previous work that used hydrocarbon sulfoglutarate surfactants focused on water-in-oil (w/o) microemulsion system and low-surface-energy materials [29,35].

As expected, the fully fluorinated surfactant di-CF2 exhibits the lowest P_{trans} among the surfactants investigated in this study. Molecular simulation studies suggested that fluorination on the surfactant chains is the key factor for producing favorable interactions with CO_2 via quadrupolar and dispersion interactions between the surfactant tails and CO_2. Moreover, fluorocarbon chains are less attractive to each other than hydrocarbon counterparts, making them are more CO_2-philic [13–15,31,40]. Here, the use of the sulfoglutarate surfactant di-CF2GLU increases P_{trans} by approximately 30 bar at 55 °C. However, the difference is small, considering the uncertainties of approximately 20–40 bar. Earlier studies by Sagisaka et al. [37,38] also reported the minor difference in P_{trans} when exchanging sulfosuccinate with the sulfoglutarate headgroup for all examined fluorinated surfactants.

For hybrid surfactants, exchanging sulfosuccinate with the sulfoglutarate headgroup significantly affects the stabilization of the w/c microemulsion systems. Compared with the hybrid CF2/AOT14 (P_{trans} = 383 bar), the extra —CH_2- content in the hybrid CF2/AOT14GLU (P_{trans} = 232 bar) decreases P_{trans} to approximately 150 bar at 55 °C, which even approaches the level of the fully-fluorinated surfactant di-CF2 (219 bar). The significant improvement of the hybrid CF2/AOT14GLU may be related to high interfacial activity at the water-CO_2 interface. Returning to the data of γ_{cmc} in Table 2, the hybrid CF2/AOT14GLU exhibits the lowest values, which illustrates high effectivity in reducing the air-water surface tension and consequently the water-CO_2 interfacial tension [36]. This result is consistent with the arguments in [15], suggesting that surfactants with lower γ_{cmc} will be expected to stabilize w/c microemulsions formation at lower P_{trans} values.

3.3. UV–vis spectroscopy measurement of w/c microemulsions

To gain evidence for w/c microemulsion formation, the presence of reverse micelles in sc-CO_2 was shown by determining the incorporation a polar water-soluble probe dye methyl orange (MO) in the water/surfactant/CO_2 systems. (MO is insoluble in sc-CO_2 and soluble in water.) The existence of reverse micelles in sc-CO_2 is indicated by the red dyed single-phase mixtures because the MO dissolves inside surfactant-stabilized water pools of the CO_2 continuous phase [44]. The UV–vis absorption spectra of MO in the water/surfactant/CO_2 systems are shown in Fig. 3. With the aforementioned phase behaviour studies, the fluorinated surfactants di-CF2 exhibit the highest and MO broad peak absorbance.

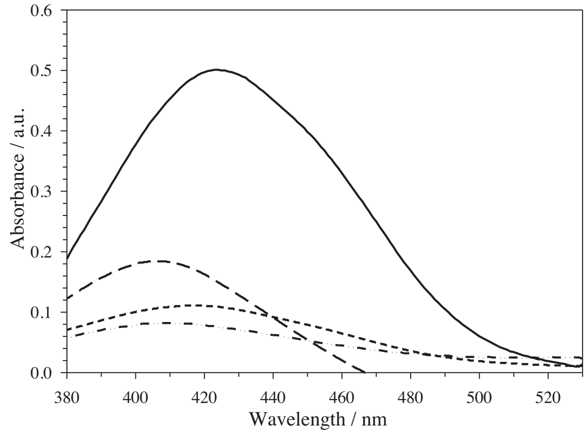


Fig. 3. UV–vis absorption spectra of methyl orange (MO 0.1 wt% in water) in surfactant/sc-CO_2 mixtures for 0.05 mol dm^{-3} surfactant at $w = 10$. The lines —; — —; – –; —••— respectively denotes for di-CF2, hybrid CF2/AOT14GLU, di-CF2GLU, and hybrid CF2/AOT14 surfactant. The experimental temperature and pressure were 45 °C and 400 bar, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

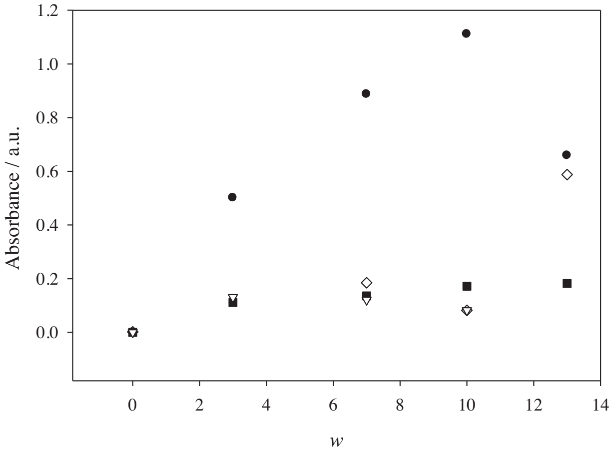


Fig. 4. Change of the maximum absorbance of MO (0.1 wt% in water) for mixtures of 0.05 mol dm^{-3} surfactant and sc-CO_2 with various w ratios at 416 nm. The symbols ●, ◇, ■, ▽, respectively denote di-CF2, hybrid CF2/AOT14GLU, di-CF2GLU, and hybrid CF2/AOT14 surfactant. The experimental temperature and pressure were 75 °C and 400 bar, respectively.

The comparisons among hybrid surfactants show that the sulfoglutarate version provides better CO_2-compatibility, as reflected by the higher absorbance of the hybrid CF2/AOT14GLU.

The solubilization of MO in water-CO_2 microemulsions is expected to display a linear relationship for MO absorbance and w up to a certain w value, as shown in Fig. 4. As observed, the increase in w gradually decreases, which suggests the phase transition from Winsor IV (1Φ) to Winsor II (2Φ) microemulsions. Following the similar lines [36–38], the trend of increasing solubilizing power is also observed when sulfosuccinate is changed for sulfoglutarate. For a CO_2-philic surfactant to have high solubilizing power, structural disorder in the surfactant molecular structure is required to decrease the length-to-breadth ratio, which decreases the possibility of liquid-crystal-like formation [36,50]. Although w_{max} is larger for the nFG(EO)$_2$ series [36–38], here, the sulfoglutarate version provides slightly higher solubilizing power than the normal sulfosuccinates di-CF2 ($w_{max} = 10$) and hybrid CF2/AOT14 ($w_{max} = 3$). Using the sulfoglutarate surfactant increases the solubilizing power of di-CF2GLU and hybrid CF2/AOT14GLU to $w_{max} = 13$ and $w_{max} = 7$, respectively. Instead of enhancing the surfactant solubilizing power, swapping sulfosuccinate for the sulfoglutarate headgroup affects the surfactant efficiency in stabilizing the w/c microemulsion more, particularly with the hybrid surfactant.

4. Conclusions

To further explore the molecular design requirements for CO_2-philic surfactants, three classes of custom-made AOT-derived surfactant–sulfoglutarate surfactants were successfully synthesized. Prior studies using selected fluorinated surfactants have shown that the sulfoglutarate versions pose a remarkable improvement in term of surfactant solubilizing power (w_{max}), although the difference in the P_{trans} considered being minor [36–39]. Here, the results show that the extra $-CH_2$ content in the surfactant headgroup causes different effects for different surfactant types. Similar with the previous studies [36–39], the differences in P_{trans} and γ_{cmc} are indeed subtle considering the involved uncertainties. Conversely, a significant $-CH_2$- head group spacer effect was observed for the hybrid surfactants. The hybrid CF2/AOT14GLU is more CO_2-philic than the parent hybrid CF2/AOT14 as indicated by the lower P_{trans} and γ_{cmc} values. Not all $-CH_2$- groups that are added to the hydrophilic headgroup contribute equally to the surfactant CO_2-philicity. The obtained results may be used as a reference to design a new generation of low-fluorine-content-based CO_2-philic surfactants.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.supflu.2016.04.018.

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