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Economical and Efficient Hybrid Surfactant with Low Fluorine Content for the Stabilisation of Water-in-CO_2 Microemulsions

Azmi Mohamed[a,b,*], Tretya Ardyani[a], Masanobu Sagisaka[c], Shinji Ono[c], Tsuyoshi Narumi[c], Makoto Kubota[c], Paul Brown[d], Craig James[c], Julian Eastoe[e], Azlan Kamari[a,b], Norhayati Hashim[a,b], Illyas Md Isa[a,b], Suriani Abu Bakar[b]

[a] *Department of Chemistry, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjong Malim, Perak, Malaysia*
[b] *Nanotechnology Research Centre, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjong Malim, Perak, Malaysia*
[c] *Department of Frontier Materials Chemistry, Graduate School of Science and Technology, Hirosaki University 1-Bunkyo-cho 3, Hirosaki, Aomori 036-8561, Japan*
[d] *Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, United States*
[e] *School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, United Kingdom*

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ABSTRACT

The relationship between the tail architecture and performance of hybrid AOT analogue surfactants has been investigated. Three hybrid surfactants were synthesised using hydrocarbon CO_2-philic tails with different levels of chain branching. The performance of each surfactant was investigated via high-pressure phase behaviour, UV-visible spectroscopy, and air–water (a/w) surface tension measurements. Notably, the incorporation of hydrocarbon CO_2-philic tails with a high degree of branching has been found to significantly boost CO_2-philicity, allowing the surfactant to stabilise water-in-CO_2 (w/c) microemulsions at low cloud pressures, P_{trans}. The newly synthesised hybrid CF2/SIS1 (sodium (*4H, 4H, 5H, 5H, 5H*-pentafluoropenyl-5,7,7-trimethyl-2-(1,3,3-trimethyl-buthyl)-octyl)-2-sulfosuccinate) is a CO_2-philic surfactant that contains the lowest amount of fluorine (15.01 wt%) and exhibits the highest efficiency of any di-chain surfactant to date. High-pressure phase behaviour studies provided a maximum water-to-surfactant molar ratio (w_{max}) of $w_{max} = 39$, which is usually only observed from surfactants with long fluorocarbon chains. The present results are beneficial for expanding the pool of economical, effective, and efficient surfactants available for CO_2-based technology.

1. Introduction

Considering the detrimental effect volatile organic compounds (VOCs) have on the environment, the number of investigations aimed at developing "greener" solvent media has increased in recent years [1–8]. One promising substitute solvent is supercritical carbon dioxide (sc-CO_2) [8,9]. Compared to traditional VOC solvents such as hexane, formaldehyde and butane, the lower critical temperature ($T_c = 31.1\,^{\circ}C$) and pressure ($P_c = 72.8$ bar) of sc-CO_2 offers benefits as an environmentally preferable solvent, as regulated by the United States Environmental Protection Agency (USEPA) [3,10–12]. As a result, interest in the utilisation of sc-CO_2 has increased substantially, as indicated by the growing number of papers published on this topic [13–25]. However, the development of sc-CO_2 as a viable universal solvent is hindered due to its non-polar nature, in which polar and/or high molecular weight compounds are sparingly soluble or fully insoluble in sc-CO_2 [10,26]. The solvency of sc-CO_2 could be improved by encapsulating polar compounds in a CO_2-continous phase by using CO_2-philic surfactant to form water-in-CO_2 (w/c) microemulsions [26,27].

Significant efforts have been devoted to designing CO_2-philic surfactants because relatively few of the commercially available surfactants are able to stabilise w/c microemulsions [28–31]. To date, fully fluorinated surfactants are identified to be the most efficient surfactants for stabilising w/c microemulsions [32–38]. The excellent performance of fluorinated surfactants is measured by two main indicators, namely, low cloud pressures (P_{trans}) and the amount of water solubilised in w/c microemulsions (w or w_c)

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* Corresponding author at: Department of Chemistry, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjong Malim, Perak, Malaysia. Tel.: +601548117582; fax: +601548117296..
E-mail address: azmi.mohamed@fsmt.upsi.edu.my (A. Mohamed).

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[33,34,36,39]. P_{trans} is the pressure at a given composition and temperature that maintains a distinct microemulsion with one phase (1Φ). Below the P_{trans}, phase separation occurs producing a mixture that is visibly turbid, which indicates a phase transition from a microemulsion (1Φ) to a macroemulsion (2Φ). The water-to-surfactant molar ratio $\left(\text{i.e., } w = [\text{water}]_{\text{dispersed}}/[\text{surfactant}]\right)$ is used to indicate the amount of water dispersed in the w/c system. Meanwhile w_c represents the corrected water-to-surfactant molar ratio in w/c microemulsions:

$$w_c = \frac{[\text{water}]_{\text{dispersed}} - [\text{water}]_s}{[\text{surfactant}]} = w - \frac{[\text{water}]_s}{[\text{surfactant}]} \qquad (1)$$

where $[\text{water}]_{\text{dispersed}}$ is the number of moles of water added to the system, $[\text{water}]_s$ is the number of moles of water soluble in pure sc-CO_2 and [surfactant] is the number of moles of surfactant in the system [40,41]. However, fluorinated surfactants are both expensive (estimated at \$200/g for di-CF4) [42] and environmentally hazardous [43]. According to the USEPA, poly- and perfluoroalkyl substances are listed as hazardous substances owing to their persistence and bioaccumulation in the environment [43]. As a result of regulatory restriction, the 3 M Company, which is a major manufacturer of fluorinated substances, has discontinued the production of such substances and has substituted the long chain poly- and perfluoroalkyl substances with four chain perfluorinated carbons, which are not considered to bioaccumulate in the environment [44].

Regarding cost and environmental issues, extensive studies have been directed towards the development of cheap and biodegradable hydrocarbon CO_2-philic surfactants [40,42,45–49]. However, only a limited number of hydrocarbon surfactants have been reported that have succeeded in stabilising w/c microemulsions [30,40,50,51]. One surfactant that is still regarded highly in studies of reverse micelle formation in sc-CO_2 is the anionic surfactant Aerosol-OT (AOT) [39,46,52]. AOT (sodium bis (2-ethyl-1-hexyl) sulfosuccinate) is a commercially available surfactant that can be readily synthesised using an inexpensive hydrogenated alcohol precursor. Without co-surfactant AOT is almost insoluble and does not aggregate; however, methylation of the surfactant chain (with 3,5,5-trimethylhexanol) to give AOT4 (sodium bis (3,5,5-trimethyl-1-hexyl)-2-sulfosuccinate) was found to enhance its solubility in sc-CO_2 ($P_{\text{trans}} = 500$ bar at 33 °C; $w = 0$; $[\text{surf.}] = 0.10\ \text{mol dm}^{-3}$ [46,53]. Another promising route in the development of hydrocarbon CO_2-philic surfactants was achieved by the incorporation of the third methylated branched on the surfactant chain [42,50,51]. The tri-chain anionic surfactant TC14 (sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulfonate) was reported to be a remarkable compound that is able to form reverse micelle in sc-CO_2 in mild conditions ($P_{\text{trans}} = 160$ bar, $w = 0$, $[\text{surf.}] = 0.04\ \text{mol dm}^{-3}$ at 25 °C). Moreover, this surfactant was shown to be soluble in a wide range of solvents, including alkane, water, and sc-CO_2 [51]. More recently, success in developing hydrocarbon surfactants was achieved by using single chain isostearyl surfactants. Sodium 2-(4,4-dimethylpentan-2-yl)-5,7,7-trimethyloctyl sulfate, which we denote as SIS1 ($P_{\text{trans}} = 245$ bar, $w = 0$, $[\text{surf.}] = 0.02\ \text{mol dm}^{-3}$ at 35 °C), possesses a hyper-branched "hedgehog" tail and is a good "fluorocarbon-like" CO_2-philic group, as indicated by the large amount of water dispersed in CO_2 ($w = 50$) [40,54]. Additionally, previous studies have revealed that this hyper-branched tail, also known as an isostearic chain, is completely miscible in sc-CO_2 and is a good candidate for nanomaterial processing [20,55]. Despite its interesting performance, SIS1 still requires relatively high temperature (>55 °C) and pressure (>210 bar) to stabilise w/c microemulsions [40].

Further attempts to develop CO_2-philic surfactants include combining separate hydrocarbon and fluorocarbon chains featuring the same headgroup. Such surfactants are known as hybrids because they are comprised of both hydro- and fluorocarbon chains. Hybrid surfactants offer interesting physicochemical properties, including an improved CO_2-philicity relative to purely hydrocarbon surfactants and a reduction of the amount of fluorine while retaining the ability to stabilise w/c microemulsions. Recent work by Mohamed et al. [53] demonstrated a simpler approach to prepare hybrid AOT analogue surfactants as-compared to other hybrid sulfonate surfactants e.g., F7H7 surfactant. The F7H7 (sodium 1-pentadecafluoroheptyl-1-octanesulfate) surfactant ($P_{\text{trans}} = 130$ bar, $w = 10$, $[\text{surf.}] = 0.05\ \text{mol dm}^{-3}$ at 40 °C) possesses multiple synthetic routes, which impedes its wide application in industrial applications [56–58]. To date, sodium *4H,4H,5H,5H,5H*-pentafluoropentyl-3,5,5-trimethyl-1-hexyl)-2-sulfosuccinate (Hybrid CF2/AOT4; $P_{\text{trans}} = 340$ bar, $w = 10$, $[\text{surf.}] = 0.05\ \text{mol dm}^{-3}$ at 40 °C) is the first economical hybrid surfactant containing the lowest amount of fluorine (18.8 wt%) that can stabilise w/c microemulsions.

It is of interest to understand the relationship between molecular structure and surfactant performance. A previous study by Harrison et al. [58] has noted that branching and methylation on double chain surfactants can enhance the CO_2-compatibility of the surfactant to stabilise w/c microemulsions. In addition, relative chain length was shown to have a significant impact on the phase stability of w/c microemulsions with the FmHn ($m = 7$, 8; $n = 4$, 7) series of surfactants under certain conditions ($w = 10$, $[\text{surf.}] = 0.04\ \text{mol dm}^{-3}$ at 30 °C). In these studies, it was found that the symmetric chain surfactants F7H7 ($\gamma_{\text{cmc}} = 22.1\ \text{mN m}^{-1}$; $P_{\text{trans}} = 103$ bar) and F8H8 ($\gamma_{\text{cmc}} = 21.6\ \text{mN m}^{-1}$; $P_{\text{trans}} = 83$ bar) exhibited greater efficiency in lowering the air-water surface tension, and thus in stabilising w/c microemulsions compared with the asymmetric chain surfactants F7H4 ($\gamma_{\text{cmc}} = 23.8\ \text{mN m}^{-1}$; $P_{\text{trans}} > 500$ bar) and F8H4 ($\gamma_{\text{cmc}} = 25.4\ \text{mN m}^{-1}$; $P_{\text{trans}} = 167$ bar) [56,57,59,60]. Following on from this previous work, the present paper aims to investigate the effect of hydrocarbon CO_2-philic tail structure on the performance of novel hybrid AOT analogue surfactants in stabilising w/c microemulsions. Three different (hydrocarbon) surfactants were studied, including tri-chain with methylated branched tails (TC14), highly branched tails (AOT4) and hyper branched (SIS1) tails. All were shown to be effective CO_2-philic groups able to stabilise w/c microemulsions [40,42,46,51]. To determine the effect of hydrocarbon CO_2-philic tail structure on the ability of hybrid surfactants to stabilise w/c microemulsions, the fluorocarbon chain was chosen to be di-CF2, which has been reported to provide the lowest fluorine content for di-chain surfactants to date [61]. Meanwhile, hydrocarbon CO_2-philic tails were varied using AOT4, AOT14, and SIS1. As a result, three different hybrid surfactants were synthesised and used in this study: hybrid CF2/SIS1, hybrid CF2/AOT4, and hybrid CF2/AOT14 (Table 1). As seen, all hybrid surfactants bear the di-CF2 tail and the primary difference between them is the hydrocarbon CO_2-philic tail structures, which have different levels of branching. To investigate the effect, if any, of hybridisation, comparisons were made involving the properties of related hydrocarbon (AOT14, AOT4, and di-SIS1), fully fluorinated (di-CF2), and equimolar mixtures of surfactants. The stable formation of w/c microemulsions by surfactants with a minimum amount of fluorine is of significant industrial interest because of cost and the detrimental effects of long-chain fluorocarbons to the environment. Notably, chemical structure modification on hydrocarbon CO_2-philic tails gives a distinct effect towards the ability of the surfactant to stabilise w/c microemulsions. Significantly, this study provides a new platform for generating economical, efficient and non-bioaccumulative hybrid surfactants for CO_2-based technology.

Table 1
Chemical Structures of Surfactants Used in This Study.

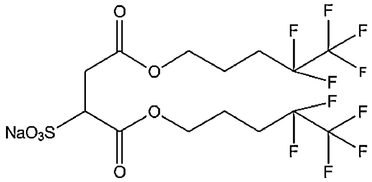
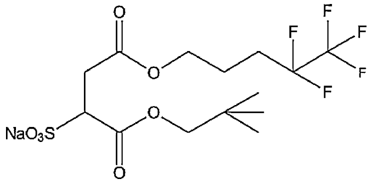
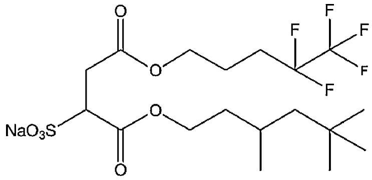
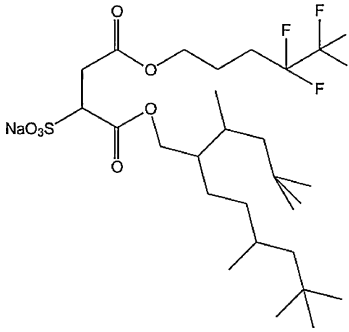
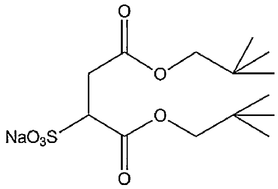
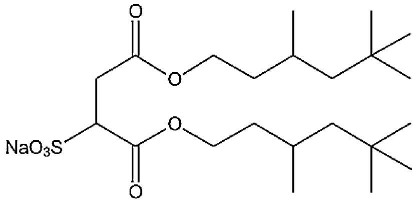
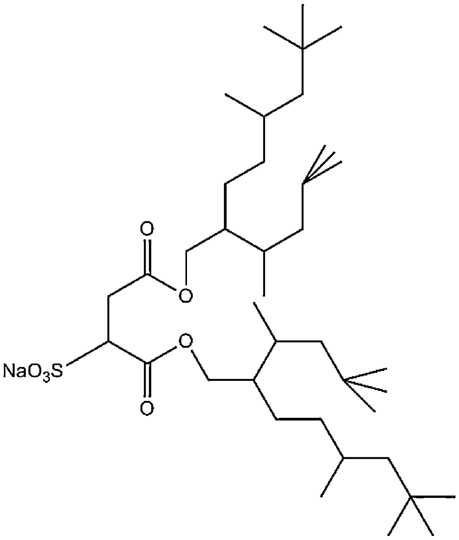
Surfactant	Structure	Chemical Name
di-CF2		Sodium bis (*4H,4H,5H,5H,5H*-pentafluoropentyl)-2-sulfosuccinate
Hybrid CF2/AOT14		Sodium (*4H,4H,5H,5H,5H*-pentafluoropentyl-2,2-dimethyl-1-propyl)-2-sufosuccinate
Hybrid CF2/AOT4		Sodium (*4H, 4H, 5H, 5H, 5H*-pentafluoropenyl-3,5,5-trimethyl-1-hexyl)-2-sulfosuccinate
Hybrid CF2/SIS1		Sodium (*4H, 4H, 5H, 5H, 5H*-pentafluoropenyl-5,7,7-trimethyl-2-(1,3,3-trimethyl-butyl)-octyl)-2-sulfosuccinate
AOT14		Sodium bis (2,2-dimethyl-1-propyl)-2-sulfosuccinate
AOT4		Sodium bis (3,5,5-trimethyl-1-hexyl)-2-sulfosuccinate)

Table 1 (*Continued*)

Surfactant	Structure	Chemical Name
di-SIS1		Sodium bis (5,7,7-trimethyl-2-(1,3,3-trimethyl-buthyl)-octyl)-2-sulfosuccinate

2. Experimental

2.1. Materials

di-CF2, di-SIS1, AOT4, and AOT14 were synthesised using the same method as reported previously [50,61]. Hybrid CF2/AOT14, hybrid CF2/AOT4, and hybrid CF2/SIS1 were prepared following strategies based on previous work [53] and are described in Section 2.2 for convenience. To add to the validity and reproducibility of this approach, the new hybrid CF2/AOT4 was synthesised and compared to previous synthetic methods. Neopentyl alcohol 98% (Acros Organics), 3,5,5-trimethylhexanol 85% (ChemAR), *4H, 4H, 5H, 5H, 5H*-pentafluoropentanol (Apollo Scientific), and FO 180 alcohol were obtained from Nissan Chemical Industries and used without further purification. Ultrapure water with a resistivity of 18.2 M Ω cm, obtained from a Millipore Milli-Q Plus system, was used in the experiments. CO$_2$ 99.99% purity (Nippon Ekitan Co., Ltd.) and methyl orange (MO; Acros Organics) were used without further treatment.

2.2. Surfactant synthesis

2.2.1. Synthesis of hybrid diester

CF2-monoester was produced by reacting maleic anhydride (2.0 eq.) with *4H, 4H, 5H, 5H, 5H*-pentafluoropentanol (1.0 eq.) overnight under reflux conditions at 80 °C. The mixture was then dissolved in diethyl ether (200 ml) and washed sufficiently with a HCl solution with pH ± 3. Pure CF2-monoester was obtained as a transparent liquid after solvent removal using a rotary evaporator.

CF2-monoester (1.0 eq.) was then reacted overnight with hydrocarbon alcohol (1.0 eq.), *p*-toluene sulfonic monohydrate (0.2 eq.), and toluene (175 ml) using a Dean and Stark apparatus to produce the hybrid diester. Water was removed azeotropically during the reaction to shift the chemical equilibrium and was used as the indicator to determine when the reaction was complete. The reaction was considered complete if the water collected in the trap was comparable to the theoretical value. The obtained diester was then washed using warm water (70 °C) to remove the *p*-toluene sulfonic monohydrate. Solvent removal was performed using a rotary evaporator. The diester that was obtained was a dark yellow liquid.

2.2.2. Sulfonation

The resulting diester (1.0 eq.) was first dissolved using ethanol (110 ml) and water until saturation. Sodium hydrogen sulfite (4.0 eq.) was added to the mixture and the reaction was carried out for 71 h under stirred and heated conditions to produce the hybrid surfactant. Surfactant formation was monitored using TLC with ethyl acetate as the eluent, which shows the presence of a spot in the baseline ($R_f \sim 0$). The reaction was considered complete with the disappearance of the diester spot at $R_f \sim 0.9$. Crude surfactant was obtained after removing the solvent by rotary evaporation and drying the product overnight in an oven at 80 °C.

2.2.3. Purification of hybrid surfactant

The first step of purifying the crude surfactant was achieved by dissolving the crude product in dried acetone. Inorganic impurities were removed by centrifugation (Sartorius Sigma) at 5200 rpm using a minimum amount of solvent. A solid material was obtained after solvent removal by a rotary evaporator. This process was repeated until no further impurities were left. Pure surfactant was left to dry overnight in an oven at 70 °C and obtained as a white yellowish powder (average yield: 60%).

2.2.4. Hybrid CF2/AOT14

^{1}HNMR (500 MHz, CDCl$_3$, TMS), (δ_H/ppm) 0.76–1.00 (a, doublet (d), 9H, $J = 4.0$ Hz), 1.81–1.87 (b, multiplet (m), 2H), 1.99-2.20 (c, m, 2H), 3.07–3.30 (d, m, 2H), 3.64–3.89 (e, m, 2H), 4.04–4.28 (f, triplet (t), 2H, $J = 6.85$), 4.31–4.41 (g, m, 1H). Elemental analysis: found C, 36.60; H, 5.29; S, 7.89. Calcd C, 37.34; H, 4.48; S, 7.12.

2.2.5. Hybrid CF2/AOT4

^{1}HNMR (500 MHz, CDCl$_3$, TMS), (δ_H/ppm): 0.77–0.89 (a, m, 12H), 1.17–1.24 (b, m, 2H), 1.40–1.60 (c, m, 4H), 1.88–2.17 (d, m, 3H), 3.05–3.24 (e, m, 2H), 4.03–4.15 (f, m, 4H), 4.26–4.33 (g, m, 1H). Elemental analysis: found C, 42.14; H, 6.00; S, 5.28. Calcd C, 42.69; H, 5.57; S, 6.33

2.2.6. Hybrid CF2/SIS1

^{1}HNMR (500 MHz, CDCl$_3$, TMS), (δ_H/ppm) 0.85–0.90 (a, m, 24H), 0.97–1.29 (b, m, 8H), 1.39–1.80 (c, m, 3H), 1.83–1.99 (d, m, 2H), 2.02–2.22 (e, m, 2H), 3.04–3.23 (f, m, 2H), 3.82–4.19 (g, m 4H), 4.27–4.32 (h, m 1H). Elemental analysis: found C, 52.17; H, 9.03; S, 4.89. Calcd C, 51.26; H, 7.33; S, 5.07.

2.3. Surface Tension Measurements

Surface tensiometry at the air–water (a/w) interface were carried out using a Wilhelmy tensiometer (CBVP-A3, Kyowa Interface Science) equipped with a platinum plate at 25 °C. Detailed information of the measurement can be found elsewhere [40,62]. Critical micelle concentrations (*cmc*) of surfactants were obtained from the break-point of the graph of surface tension (γ) versus ln of concentration (ln c).High Pressure Phase Behaviour and UV-Visible Absorption Measurements

The phase behaviour and w/c microemulsion formation of the surfactants were examined visually and with UV-visible spectroscopic measurements. The measurements were carried out at temperatures ranging from 35 °C to 75 °C in the mixture of CO_2/water/surfactant. Surfactants (0.05 mol dm^{-3}) and CO_2 were loaded into the optical cell and stirred for 1 day to form a clear transparent single phase. A known volume of water or aqueous methyl orange solution was then loaded into the mixture and the pressure was varied until the clear transparent single phase Winsor IV became turbid macroemulsions. Detailed information of the experimental apparatus and procedure can be found elsewhere [41,63].

3. Results and discussion

3.1. Surface tension measurement

Using fluorinated analogues of the AOT series of surfactants, Eastoe et al. [66] demonstrated a clear correlation between the air–water surface tension lowering ability (i.e. γ_{cmc}) and the ability of these surfactants to stabilise w/c microemulsions. Measurement of the air–water interface can be used as a reference that can be compared to the lower range of the water-CO_2 interface, which is typically 20–30 mN m^{-1}[62,67–69].

The pre-cmc data were fitted to quadratics to calculate the adsorption isotherm using the Gibbs equation (Eq (2)). Thus, the effective area per molecule at the critical micelle concentration (*cmc*) (A_{cmc}/Å^2) is obtained as follows:

$$\Gamma = -\frac{1}{m\mathrm{RT}}\frac{\mathrm{d}\gamma}{\mathrm{dlnc}} \quad (2)$$

$$A_{\mathrm{cmc}} = \frac{1}{\Gamma N_{\mathrm{A}}} \quad (3)$$

where $m = 2$ for ionic surfactants and a prefactor of 1:1 corresponds to the fully dissociating ions [70]. The *cmc*, limiting surface tension (γ_{cmc}), and A_{cmc} derived from the surface tension graph are listed in Table 2.

Surface tension data for di-CF2, AOT14, AOT4, hybrid CF2/AOT14, hybrid CF2/AOT4, and hybrid CF2/SIS1 are plotted as a function of surfactant concentration (Fig. 1). There is an obvious trend of decreasing *cmc* values with increasing effective chain length as those reported previously [51,54,57,64]. Here, the effective chain length considers only the longest linear hydrocarbon CO_2-philic tail for both hybrid and hydrocarbon surfactants. Interestingly, increasing the number of carbon on the hydrocarbon CO_2-philic tails via chain branching was also found to significantly increase the surfactants hydrophobicity.

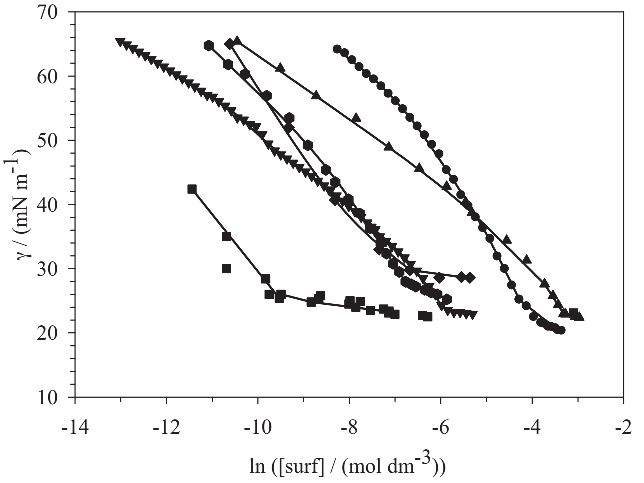


Fig. 1. The changes of air-water surface tension as a function of ln surfactant concentration at 25 °C. Quadratic lines fitted to the pre-cmc data are shown. The closed symbols ●, ▲, ♦, ⬢, ▼, ■ respectively denotes for di-CF2, hybrid CF2/AOT14, AOT14, AOT4, hybrid CF2/AOT4 and hybrid CF2/SIS1 surfactant.

The limiting surface tension (γ_{cmc}) value of a CO_2-philic surfactant represents the effectiveness of the surfactant to reduce air-water surface tension ($\gamma_{a/w}$). Of the surfactants examined in this study, the fluorinated surfactant di-CF2 exhibited the lowest and most effective capacity to reduce $\gamma_{a/w}$ (up to 22.4 mN m^{-1}). This is typical for fluorinated surfactants, which are recognised widely for their ability to lower $\gamma_{a/w}$ to extreme values [33,35,66,71]. This low γ_{cmc} is attributed to fewer intermolecular interactions between the fluorocarbon chains [72,73]. Hybridisation of di-CF2 to hybrid surfactants modifies the γ_{cmc} value of the hybrid surfactant series, e.g., for hybrid CF2/SIS1, γ_{cmc} = 26.0 mN m^{-1}. This is may be attributed to the decreasing level of fluorination on the surfactant. It is believed that the ability of surfactants to reduce $\gamma_{a/w}$ is well correlated with the level of fluorination on the surfactant, as reported previously [57,59,61].

The non-hybrid hydrocarbon surfactants AOT14 (γ_{cmc} = 28.6 mN m^{-1}) and AOT4 (γ_{cmc} = 28.0 mN m^{-1}) exhibited higher γ_{cmc} values compared to the fluorinated surfactant di-CF2. Measurements involving di-SIS1 were not possible at the temperature used in this study because of its high Krafft point ($K_p \geq 56$ °C) [54,65]. The high Krafft point is indicative of a more hydrophobic surfactant, which causes the surfactant to be insoluble in water at 25 °C. Compared to the linear chain hydrocarbon surfactants, which commonly possess γ_{cmc} values of 30–40 mN m^{-1}, the results obtained here are much lower [64]. Branching and methylated tips affect the ability of the surfactants to reduce surface tension by lowering tail-tail interactions and therefore the surface energy [39,46,74]. As reported previously, the ability of the chain tips to reduce the value of γ_{cmc} follow the trend: $CF_3 > CF_2 > CH_3 > CH_2$ [74]. Partial fluorination on fully hydrocarbon surfactants to give the hybrid surfactant CF2/AOT14, for example, increases the ability of the surfactant to reduce surface tension below 23 mN m^{-1}. Apparently, fluorination on the molecular structure of the surfactant is a key factor to achieve lower γ_{cmc} values whilst at the same time improving the CO_2-compatibility [53,61].

3.2. Phase behaviour and UV-Visible spectroscopy studies of w/c microemulsions

Observation of phase behaviour is necessary for microemulsion studies because they give insight into the ability of the surfactants to solubilise water in a CO_2-continuous phase at optimum conditions [75]. For a comparable study, measurements were conducted at a fixed surfactant concentration of 0.05 mol dm^{-3}, w = 10 and temperature (35–75 °C). Phase behaviour and P_{trans}, which is the pressure to occur transition from transparent single phase (1Φ) to

Table 2
Surfactants Properties in CO_2 and Parameters Derived from Surface Tension Measurement at 25 °C.

Surfactant	Fluorine/wt%	Branching Factor	cmc[a]/(mmol/dm^3)	γ_{cmc}[b]/mN m^{-1}	A_{cmc}/Å^2	P_{trans}[c]/bar (±40 bar)
di-CF2[d]	35.16	4.8	19.0	22.4	65	219
Hybrid CF2/AOT14	21.09	3.4	46.8	22.5	102	383
Hybrid CF2/AOT4[d]	18.76	3.9	3.30[d]; 1.78	23.5[d]; 23.8	71[d]; 103	321
Hybrid CF2/SIS1	15.01	4.9	0.05	26.0	112	215
AOT14	0.0	2.0	2.39	28.6	100	Incompatible
AOT4[e]	0.0	3.0	1.10	28.0	70	Incompatible
di-SIS1	0.0	5.0	–	–	146[f]	Compatible

[a] Critical micelle concentration.
[b] Surface tension at cmc.
[c] P_{trans} is the observed reversible cloud-point pressure in CO_2 or observation on surfactant solubility at $w = 10$, w/c, 55 °C.
[d] Data collected by Mohamed [53,61].
[e] Data collected by Nave [64].
[f] Data collected by Sagisaka [65].

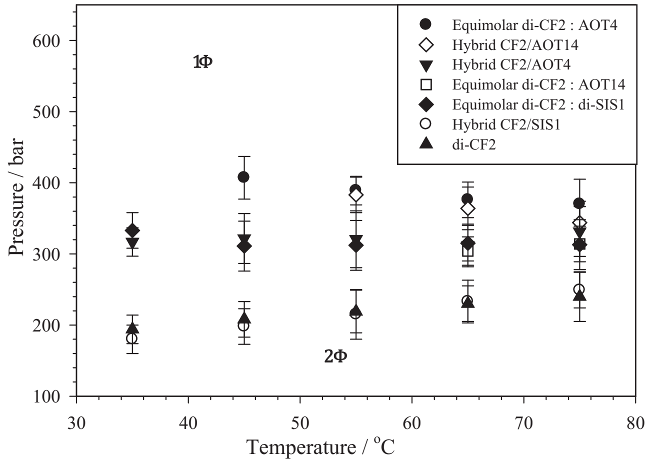


Fig. 2. Phase behaviour of surfactants in CO_2 at various temperature for 0.05 mol dm^{-3} surfactant and water-to-surfactant molar ratio (w) = 10. The 1Φ and 2Φ denotes for microemulsion and macroemulsion phase respectively. The error bars represent the uncertainty of P_{trans} (±40 bar).

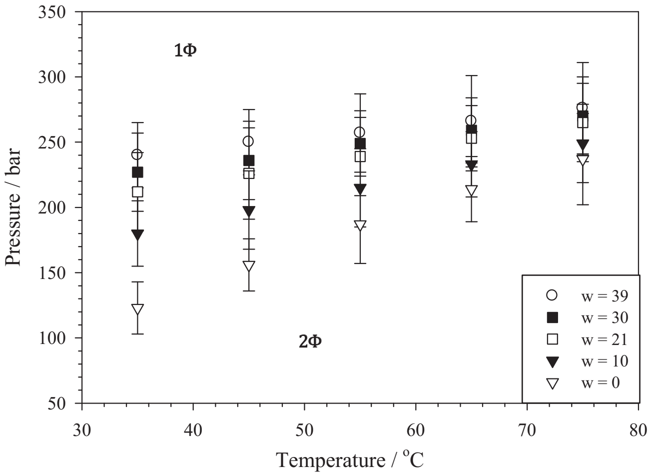


Fig. 3. Phase behaviour of 0.05 mol dm^{-3} hybrid CF2/SIS1 in CO_2 at various temperature and water-to-surfactant molar ratio (w). The 1Φ and 2Φ denotes for microemulsion and macroemulsion phase respectively. The error bars represent the uncertainty of P_{trans} (±40 bar).

turbid two phase (2Φ), for the surfactants used in this study are presented in Fig. 2 and Table 2, respectively.

Of the hydrocarbon surfactants examined, it was found that AOT4 and AOT14 were not able to stabilise w/c microemulsions at $w > 0$. For this reason, data involving these surfactants are not shown in the phase diagram. As previously reported, AOT4 appears to form a dry reverse micelle in CO_2. However, the incorporation of *t*-butyl tips on the surfactant chain was not sufficient to microemulsify water in CO_2 [46,50]. Meanwhile, the di-SIS1 surfactant was found to be compatible in CO_2 with a high cloud pressure (estimated $P_{trans} > 400$ bar).

On the other hand, the fluorinated surfactant di-CF2 exhibited the lowest cloud pressure among the surfactants examined in this study. This result is consistent with other fluorinated surfactants in other w/c systems [4,33,35,39,61,66]. The fluorocarbon chain demonstrated high CO_2-philicity owing to weak intermolecular interactions, which consequently provide a strong quadrupolar interaction with CO_2 [76]. Numerous papers have also reported that the distinguishing feature of fluorocarbon chain is the better partitioning between water and CO_2 [61,76–78]. A fluorocarbon chain (516 Å^3) is significantly larger than a hydrocarbon chain (361 Å^3) at the interface, which is proposed to block the interpenetration between water and CO_2 molecules to avoid phase separation [61,76–78].

Substitutions of a di-CF2-tail ($CF_3CF_2CH_2CH_2CH_2$-) for one of double hydrocarbon tails to yield hybrid surfactants had a significant impact on the ability of the surfactant to stabilise the w/c microemulsion system. Notably, the exchange of one surfactant tail to di-CF2 tail allowed the surfactant to stabilise the w/c microemulsion at 383 bar ($T = 55$ °C; $w = 10$). Indeed, fluorination is necessary to achieve the CO_2-compatibility of the surfactant chain [37,61,71].

The phase stability of the w/c microemulsion system has been shown to be quite sensitive to subtle changes of the surfactant tail structure, which affects its compatibility with CO_2 [56,66,71,79]. Fluorination, branching and methylation tips have been shown to weaken the intermolecular interactions between tails and consequently enhance the CO_2-compatibility of the surfactant chain [39,46,49,68,80]. Compared to hybrid CF2/AOT4, the introduction of the short, methylated and branched AOT14 tail on hybrid CF2/AOT14 has been shown to increase the P_{trans} to approximately 60 bars at 55 °C. Interestingly, exchanging the AOT4 tail with a hyper-branched stearyl tail on hybrid CF2/SIS1 ($P_{trans} = 215$ bar) modifies the performance of the surfactant to become more like the fluorinated surfactant di-CF2 ($P_{trans} = 219$ bar). This surfactant was also suggested to yield 1Φ up to $w = 39$ by visual observation (Fig. 3), which could be the highest value reported for hybrid surfactants in a w/c microemulsion system [41,56], if all water molecules at $w = 39$ were solubilized in the micelles. Hybrid CF2/SIS1 possesses a hyper-branched stearyl tail that has been shown to have an effective interaction with CO_2 [40,55]. More recently, this hedgehog tail has been shown to possess low surface energy, which is an important feature for developing CO_2-philic surfactants with high solubilising power [54,65].

To investigate the effect of FC-HC hybridisation of surfactant tail on microemulsion phase stability, comparisons were made

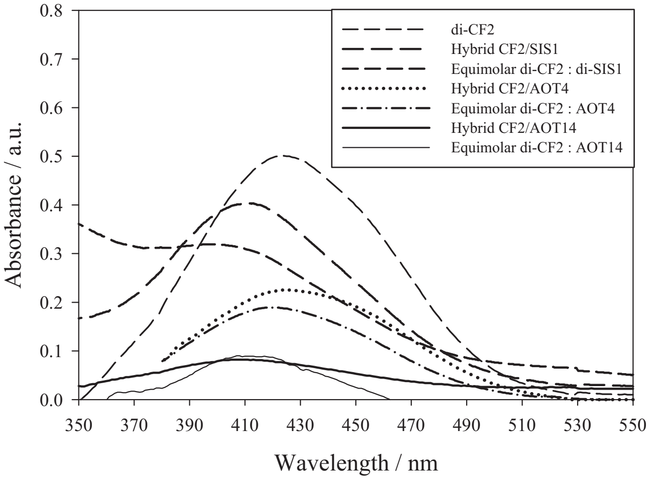


Fig. 4. UV-visible absorption spectra of MO (0.1 wt% in water) in surfactants/sc-CO_2 mixtures for 0.05 mol dm^{-3} surfactant at w = 10. The experimental temperature and pressure were at 45 °C and 400 bar, respectively.

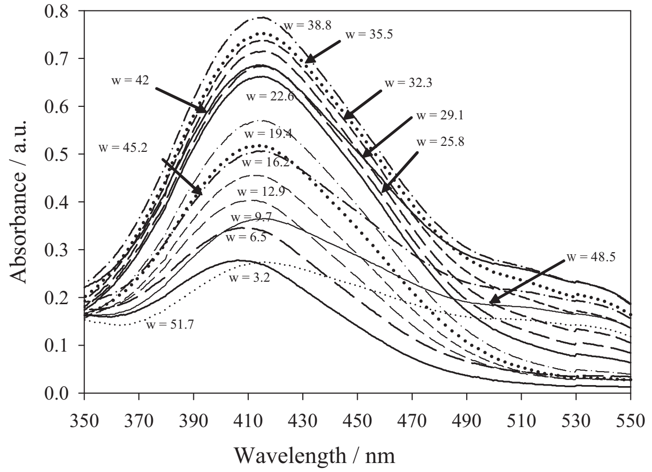


Fig. 5. UV-visible absorption spectra of MO (0.1 wt% in water) in hybrid CF2/SIS1/sc-CO_2 mixtures for various w ratios. The experimental temperature and pressure were at 75 °C and 400 bar, respectively.

between hybrid surfactants and equimolar mixtures of the related hydrocarbon and fluorinated surfactants, e.g., hybrid CF2/SIS1 and equimolar di-CF2:di-SIS1. It is clear that hybridisation on hybrid surfactants gives much lower P_{trans} compared to the mixed surfactant system for approximately 100 bar at w = 10 and T = 55 °C. The present results are in good agreement with previously reported values involving the same surfactant template [53]. Significantly, hybridisation on the surfactant chain gives positive synergistic effects, while the mixed surfactant system does not, which is difficult to rationalise [81,82]. Indeed, the present results provide a promising development for hybrid surfactants as a substituent for highly fluorinated surfactants, which are considered to bioaccumulate in the environment.

To ascertain the solubilising power of each surfactant used in this study, the formations of w/c microemulsions were investigated by visually observing the solubilisation of an aqueous dye (methyl orange solution) in the water-CO_2-surfactant systems [63]. Methyl orange (MO) does not dissolve in sc-CO_2. However, on formation of reverse micelles (w/c microemulsions) the MO solution is loaded into the dispersed aqueous phase and is coloured red [63]. Fig. 4 shows the UV-visible absorption spectra of methyl orange solution in the w/c system for the surfactants used in this study. Among the hybrid surfactants studied, hybrid CF2/SIS1 gives the highest and broadest peak absorbance at (415 nm). The broad peak absorbance gradually increases until $w \sim 39$ (Fig. 5). As reported previously [35,36,53], proportional solubilisation of MO solution in w/c microemulsion gives the linear relationship between absorbance and w until reach certain w value (Fig. 6). Fig. 5 and Fig. 6 give evidences the decrease of absorbance at w greater than 39, suggesting the transition of Winsor IV (1Φ) into Winsor II (2Φ) microemulsions with excess separated water. Importantly, this result indicates a high MO uptake by the w/c system and suggests that the low fluorine content hybrid CF2/SIS1 clearly outperform all the hybrid surfactants considered [41,53,56–58]. The high water solubilisation (up to w ∼ 39) is the more remarkable since this hybrid CF2/SIS1 contains lowest amount of fluorine (15.01 wt%) for any hybrid di-chain surfactants to date [33,36,41,53,56–58,61]. Compared to the mixed surfactant system, hybrid surfactants exhibit a higher microemulsifying ability and are consistent with the lower P_{trans} values. The results obtained here are also in a good agreement with those previously studied on the same surfactant template in a w/c system [53].

Interestingly, incorporating the hydrocarbon CO_2-philic tails with different levels of branching shows a close link of the ability of the surfactant to stabilise w/c microemulsions. Further explanation will be needed to understand the relationship between branching level and surfactant performance to generate efficient CO_2-philic surfactants with low fluorine content.

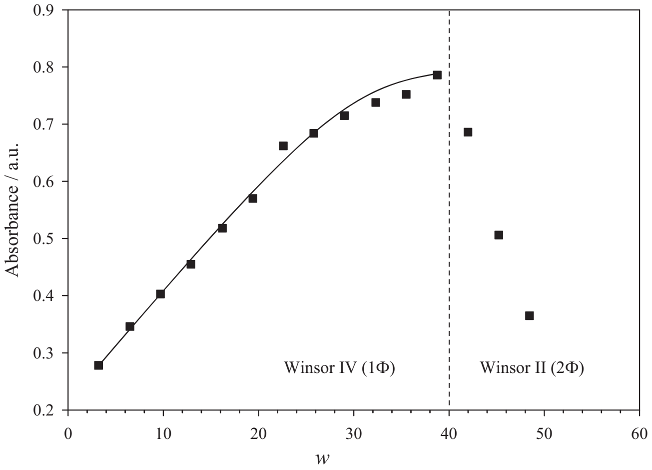


Fig. 6. Change of the maximum absorbance of MO (0.1 wt% in water) for hybrid CF2/SIS1/sc-CO_2 mixtures with various w ratios. The surfactant concentration was 0.05 mol dm^{-3} in CO_2. The experimental temperature were 75 °C and 400 bar, respectively. The 1Φ and 2Φ respectively denotes for Winsor IV microemulsion and Winsor II macroemulsion phase.

3.3. *Optimising CO_2-philic surfactants performances via chain branching*

The molecular structure of surfactants has been shown to play a key role in promoting the efficiency of the surfactant to stabilise w/c microemulsions [39,68,77,78,83]. Numerous papers have noted that certain structural modification (e.g., fluorination, branching and methylation on the surfactant tail) can vastly improve the CO_2-philicity of surfactants [39,46,58,61,67,78]. With regard to chain branching, experimental and simulation studies have been conducted to rationalise how branching of the surfactant chain can improve the surfactant performance in CO_2 [46,67,78,83]. Branching has been shown to increase the tail-CO_2 interactions by limiting the number of intermolecular interactions between the surfactant tails and consequently leading to a greater affinity towards CO_2-continuous phase, namely, low hydrophilic–CO_2-philic balance (HCB) [49,67,84]. CO_2-philic surfactants with low HCB value possess greater tendency to favour bending about water, thus give stable w/c microemulsions formation [49,67,84].

The level of branching on the surfactant chain can be quantified with a branching factor [54,64,85]. A previous study by Tabor et al. [85] has devised a branching factor calculation that considers the effects of both length and branching position on the surfactant chain. The branching factor is defined as [85]:

$$\text{Branching factor} = \frac{(\text{branch length} \times \text{branch position})}{\text{number of carbon}} \quad (4)$$

The branching factor for AOT4, for example, was calculated as follows: 1 methyl in position 3 and 3 methyls on position 5 on a C_6 linear chain, i.e., $(1 \times 1 \times 3) + (3 \times 1 \times 5)/6 = 3$. Methyl tips are counted as methyl branches on the penultimate carbon, which in this example gives three methyl branches on position 5.

Branching factors have been successfully used to understand aqueous solution properties and the effectiveness of surfactants in both a/w and o/w interfaces [54,64,65,85]. Along similar lines, increasing the chain branching of the surfactants used in this study has shown to give a significant improvement to the effectiveness in stabilising w/c microemulsions. Therefore, we also used the so-called branching factor to help understand the surfactant performance in CO_2. However, all of the previous studies mentioned focused solely on hydrocarbon surfactants. For CO_2 studies, hydrocarbon surfactants are known to be incompatible with stabilising w/c microemulsions [28], whereas fluorinated and hybrid surfactants exhibit much higher CO_2-compatibility. As a result, we propose a method for calculating branching factors for hybrid (fluorinated) surfactants.

A similar branching factor calculation as previously introduced by Tabor et al. [85] is used to scale the branching level of fluorinated surfactants. Fluorine on the surfactant chain was assumed to be similar to methyl branches on the surfactant chain. Because fluorine itself is voluminous, the contributions of F (28.39 Å^3) and CH_3 (27.4 Å^3) via a volumetric ratio are encompassed in the calculation as a multiplicative factor of 1.04. For instance, the branching factor for di-CF2 surfactant was calculated as follows: 2 fluorines on position 4 and 3 fluorines on position 5 on a C_5 linear chain, i.e., $(2 \times 1.04 \times 4) + (3 \times 1.04 \times 5)/5 = 4.8$. Furthermore, we also propose a method for quantifying the branching level of hybrid surfactants. Because hybrid surfactants combine hydrocarbon and fluorocarbon chains on the same hydrophilic headgroup, each contribution of hydrocarbon and fluorocarbon tail are summed and divided by the number of chains (e.g., divided by 2 for di-chain surfactants). Branching factors for fluorinated, hydrocarbon and hybrid surfactants used in this study are given in Table 2.

It is clear that increasing the level of branching results in a higher degree of hydrophobicity in both hybrid and hydrocarbon surfactants. Given that the hybrid series of surfactants bear the same fluorocarbon chain, the results are even more remarkable. The hydrocarbon CO_2-philic portion appears to play a role on the hydrophobicity of the surfactant. The results here suggest the hydrophobicity order as: hyper-methylated branched tail > highly methylated branched tail > short methylated branched tail.

Increasing the branching level of hydrocarbon surfactants significantly affects the CO_2-philicity of the surfactants. Of the three hydrocarbon surfactants studied, only di-SIS1 (branching factor = 5) demonstrates CO_2-compatibility. Additionally, the hybrid surfactant with the highest branching factor, i.e., hybrid CF2/SIS (P_{trans} = 215 bar), is shown to be the most efficient in stabilising w/c microemulsions. The higher branching factor suggests a bulkier surfactant tail at the CO_2-water interface. Hence, the surfactant prefers the CO_2-continuous phase and increases curvature around the water, giving a lower HCB of the surfactants, which allows for the formation of w/c microemulsions under mild conditions [49,67,84]. A similar rationale is applicable to the fluorinated surfactants.

For the hybrid series, the obtained A_{cmc} values (Table 2) follow the trend of increasing A_{cmc} value with increasing values of the branching factor, which is similar to reports by Nave et al. using a AOT series of surfactants [64]. An increase of A_{cmc} indicates that the hydrophobic portion of the surfactant occupies a relatively larger area. These results in an increase of the critical packing parameter, which is expected to enhance the ability of CO_2-philic surfactants to stabilise w/c microemulsions [67,86]. If we consider that the difference of the hybrid surfactants is due primarily to the type of hydrocarbon CO_2-philic tail, the results here highlight the role of the hydrocarbon portion on the surfactant coverage at the interface. Amongst the series, hybrid CF2/SIS1 exhibited the largest A_{cmc} because of its hedgehog isostearyl CO_2-philic tail [40,54,65]. This implies that this hyper-branched tail occupied the largest area at the interface and consequently has the highest phase stability in the w/c system [40,54,65].

All in all, the results obtained herein are in good agreement with previous studies that reported methylation and branching of the surfactant chain increases its hydrophobicity in both air–water and water–CO_2 interfaces [65,67]. Compared to surfactants with linear chains, branching and methylation tips were found to lower the cohesive energy density of the surfactants, which therefore increases their hydrophobicity and CO_2-compatibility [39,46].

4. Conclusion

Efforts to develop CO_2-philic surfactants have been on-going for several decades. One classic problem in designing an effective CO_2-philic surfactant is the high dependence of long-chain perfluorocarbons to achieve high CO_2-philicity [33,56]. The possibility of limiting the amount of fluorine on the surfactant chain provides new insight for the development of more environmentally benign surfactants [61]. The design of facile and economical hybrid AOT analogue surfactants using low fluorine content by Mohamed et al. [53] was a great step forward in the development of CO_2-philic surfactants. One remaining concern is that this hybrid is not able to stabilise w/c microemulsions in pressures lower than 250 bar and therefore has limited solubilising power.

With regards to optimising the surfactant molecular structure to possess high efficiency, three specialised hybrid AOT analogue surfactants with different hydrocarbon CO_2-philic branched tails have been successfully synthesised. It has been shown that the aqueous properties, as well as surfactant performance in CO_2, could be explained in terms of the level of chain branching. The level of branching on the surfactant chain could be quantified using the so-called branching factor. The results imply that a higher branching factor is indicative of a larger area occupied by the surfactant molecule, which is able to block the movement between water and the CO_2-continuous phase. It is important to note that the branching factor values between hydrocarbon, fluorinated and hybrid surfactants cannot be compared directly. For hydrocarbon surfactants, the utilisation of hyper-branched surfactants (branching factor = 5) appears to promote a favourable interaction between the surfactant and CO_2, allowing the surfactant to stabilise w/c microemulsions. In particular, the hydrocarbon portion seems to affect the favourable interactions between the surfactant tail and CO_2. Within the hybrid series containing the same fluorocarbon chain, incorporation of the hydrocarbon CO_2-philic tail with a high level of branching significantly enhanced the interaction between the tail and CO_2. Notably, with just two fluorinated carbons on the surfactant chain (e.g., $-CF_2CF_3$), the hybrid CF2/SIS1 was shown to be as effective and efficient as a fluorinated surfactant. Significantly, this study provides new insight for designing a complete hybrid surfactant that includes high solubilising power and low fluorine content. Therefore, it is very beneficial because it advances surfactant molecular design for green CO_2-based technology.

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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.2015.01.012.

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