Synthesis and Characterisation of Metallosurfactants as Carbon Dioxide Viscosity Modifier

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Abstract
This paper focuses on a systematic approach to enhance the viscosity of supercritical CO$_2$ (scCO$_2$) for enhanced recovery applications. Recent successful results have shown for the first time that fluorinated surfactants can be used as viscosity modifiers for CO$_2$. Although some fluorinated surfactants have been synthesised, up to now no systematic studies have been carried out toward scCO$_2$ viscosity enhancement and impeded commercial developments of viscosity modifier. Here, metallosurfactant structure design was focused on anionic surfactant analogues of Aerosol-OT (sodium bis (2-ethyexyl) sulfosuccinate). The metallosurfactant were systematically synthesised with modification centred on fluorinated content in surfactant chain with introduction of nickel (Ni$^{2+}$) and manganese (Co$^{2+}$) counter ions. The metallosurfactant have been investigated by a range of techniques including Nuclear Magnetic Resonance (NMR) Spectroscopy, UV-Visible Spectroscopy and High-Pressure Viscometer. The result shows that fluorination is a crucial factor influencing Aerosol-OT surfactant analogue compatibility with scCO$_2$. The presence of fluorine in the metallosurfactant chemical structure gives rise to relative scCO$_2$ viscosity. The results obtained are beneficial for expanding CO$_2$ in enhanced oil recovery applications and realising its potential using the most efficient metallosurfactant as CO$_2$ viscosity modifier.

Keywords: carbon dioxide, viscosity modifier, surfactant.

INTRODUCTION

Supercritical carbon dioxide (scCO$_2$) has received considerable attention as a novel solvent medium due to an easily accessible critical point, at $T_c = 31 \, ^\circ\text{C}$ and $P_c = 73 \, \text{bar}$, above which its compressibility leads to solvent qualities (e.g. dielectric constant, density) that are tuneable by T and P — a clear advantage over conventional liquid solvents [1, 2]. In contrast, many other common solvents either have much higher critical temperatures / pressures e.g. water ($T_c = 374 \, ^\circ\text{C}$ and $P_c = 221 \, \text{bar}$), toluene ($T_c = 319 \, ^\circ\text{C}$ and $P_c = 41 \, \text{bar}$); or are flammable (and therefore regulated) e.g. ethane with $T_c = 32 \, ^\circ\text{C}$ and $P_c = 49 \, \text{bar}$ [3]. Due to the low or zero heat of vaporisation of its liquid or supercritical states, scCO$_2$ is also easily recovered (and therefore recycled) after use by depressurisation, removing the requirement for solvent removal / drying steps [1]. Commercial applications of scCO$_2$ as a solvent have already been demonstrated in several industries [4], including speciality cleaning (dry-cleaning, de-greasing of high value items), extraction (decaffeination, extraction of volatile fragrance compounds), and even refrigeration for home air conditioning systems. However, these applications have so far been restricted to highly specialised, niche markets, mainly due to the poor solvent quality of this weak, non-polar solvent [5, 3]. To realise the full economic and environmental potential of scCO$_2$, creative new approaches to modify its physico-chemical properties are required, including improvement of the solvent quality by the incorporation of polar domains using surfactants or polymers [4, 3]; by influencing other solvent properties e.g. viscosity, for applications such as oil recovery [6]; or by the dispersion of e.g. catalytically active inorganic materials to form a catalytic system with facile product recovery [7, 8].
In oil and gas industry, scCO$_2$ is commonly used for fracture simulation and enhanced oil recovery (EOR). Despite the promising utilisation of sc-CO$_2$ in EOR, it is not without its own problem. The low viscosity of scCO$_2$ poses as a hindrance in terms of EOR efficiency that will affect the optimum oil production [9]. Even as fracturing fluid, this poor viscosity may become the factor of proppant settling and fluid leak-off that might give disadvantages for the process efficiency. These manifold drawbacks in applying scCO$_2$ therefore must be addressed to facilitate the CO$_2$-based industry. All this may be overcome by thickening the viscosity of scCO$_2$ [9].

During many years, studies on CO$_2$-compatible compounds hinted the promising result when fluorine is present on the compounds molecular structure. Huang and co-workers used copolymers of fluoroacrylate and styrene as modifier and they predicted up to 20-fold thickening of scCO$_2$ viscosity at copolymer concentrations around 1.0 wt %. [10]. Along similar lines, Shi and co-workers (2001) used another fluorinated compounds; fluorinated telechelic ionomer to increase the viscosity of dense CO$_2$ by 2 to 3 fold without the need of co-solvent at ionomer concentration of 2 – 4 wt% (Shi et al., 2001). Other CO$_2$ thickener based on polyfluoroacrylate polymer, was also reported to provide significant enhancement without the help of co-solvent [10, 11]. All these materials reported above, however, contained highly fluorinated compounds that are both expensive and environmentally harmful.

This paper focuses on a systematic approach to understand what molecular criteria may be used to increase the viscosity of supercritical CO$_2$ (scCO$_2$) for enhanced recovery applications. Recent successful results have shown for the first time that fluorinated surfactants can be used as viscosity modifiers for CO$_2$ [12]. Although some surfactants have been synthesised and used successfully with CO$_2$, lack of carbon dioxide viscosity enhancement properties have impeded their commercial developments. Thus, the challenge of developing fluorinated surfactants as viscosity modifiers remains a challenge. Recently, very promising low fluorne content surfactants have been identified that can stabilise water-in-CO$_2$ (w/c) microemulsions [13, 14, 15]. Interestingly, this is the first time that these transition metal counterions have been incorporated into low fluorne CO$_2$-philic surfactants or recognised as metallosurfactants and systematically studied in scCO$_2$. Thus, the introduction of transition metal counterions to low fluorne content surfactants or metallosurfactants represents an exciting new approach and experimental data are essential in order to investigate whether these compounds represent new economical and effective surfactants for scCO$_2$ viscosity enhancement in enhanced oil recovery applications.

**Table 1** Double-chain fluorinated sulfosuccinate surfactants used in this study

| Surfactant | Surfactant structure | Chemical Name |
|------------|---------------------|---------------|
| di-HCF4    | ![di-HCF4 structure](image) | sodium bis (1H, 1H, 5H-perfluoropentyl)-2-sulfosuccinate |
| di-HCF6    | ![di-HCF6 structure](image) | sodium bis (1H, 1H, 7H-perfluoroheptyl)-2-sulfosuccinate. |
| di-CF2     | ![di-CF2 structure](image) | sodium bis (4H, 4H, 5H, 5H-pentafluoropentyl)-2-sulfosuccinate. |
MATERIALS AND METHODS

Materials

All chemicals were of analytical reagent grade and used as received. Chemicals and reagents that were used as follows: Alcohol precursor: 1H, 1H, 5H-perfluoropentanol (Apollo Scientific), 1H, 1H, 7H-perfluoroheptanol (Apollo Scientific), 4H, 4H, 5H, 5H ,5H- pentafluoropentanol (Apollo Scientific); Chemical precursor: Maleic anhydride (Friendemann Schmidt), p-toluene-4-sulfonic acid monohydrate 98% (Merck), sodium hydrogen sulfite (Friendemann Schmidt), nickel (II) nitrate 98% (Sigma Aldrich), Cobalt (II) Nitrate 98% (Sigma Aldrich); Solvent: toluene 99.5% (Systerm), n-hexane 99% (Systerm), ethyl acetate 99.5% (Systerm), 1,4-dioxane 99% (Systerm), acetone 99.5% (Systerm), diethyl ether 99% (Systerm). CO2 99.99% purity (Nippon Ekitan Co., Ltd.) was used without further treatment.

Surfactant Synthesis

Synthesis of Double-chain Fluorinated Sulfosuccinate Surfactants

The experiment involved four main steps: esterification, purification of diester, sulfonation, and purification of surfactant.

Esterification

A mixture of alcohol (2.2 eq), maleic anhydride (1.0 eq), p-toluene-4-sulfonic acid monohydrate (0.2 eq), and toluene (100 mL per maleic anhydride), were heated overnight under reflux conditions using a Dean and Stark apparatus. Water was removed azeotropically during the reaction to induce a chemical equilibrium shift. The reaction was considered complete when the amount of water collected in the trap was comparable to the theoretical amount, then washed using warm water (70°C) to remove excess maleic anhydride and p-toluene-4-sulfonic acid monohydrate (0.2 eq). Solvent was removed using a rotary evaporator and the diester was obtained as a yellow liquid.

Purification of Diester (Column Chromatography)

Column chromatography was prepared by using silica powder (SiO2) with solvent (33% ethyl acetate in n-hexane). Diester was loaded into the column and flushed using the above solvent composition. Thin layer chromatography (TLC), was used to assess the composition, showed a characteristic spot about two thirds of the way along the plate. Removal of solvents was performed using a rotary evaporator. A light yellow liquid was obtained as the pure diester.

Sulfonation

The diester was first dissolved using 1,4 dioxane for the fluorinated diesters, and water was added to the mixture until saturation. Sodium hydrogen sulfite (2.0 eq), was added to the mixture and the reaction was allowed to continue for about 7–9 hours. Surfactant formation was monitored using TLC. The reaction was considered complete with the disappearance of the diester spot and the appearance of a crude surfactant spot in the baseline. Crude surfactant was obtained after solvent removal using rotary evaporation and dried overnight in an oven at 80 °C.

Purification of Surfactants

The first step of the purification was to dissolve the crude surfactant in dried acetone. The crude surfactant was dissolover whilst stirring for two hours to obtain the maximum yield. Solvent was removed using a rotary evaporator and a white solid product was obtained. Inorganic impurities were removed by centrifugation at 5200 rpm for 20 minutes. Solvent was removed from the remaining solid using a rotary evaporator. All purified surfactants were characterized using 1H Nuclear Magnetic Resonance (NMR) Spectroscopy (JEOL 550 MHz) and Elemental Analysis (Thermofinnigan).
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Preparation of (Ni\(^{2+}\) or Co\(^{2+}\)) Metallosurfactants (M\(^{2+}\)-surfactant)

Saturated solutions of metal (Ni\(^{2+}\) or Co\(^{2+}\)) nitrates were prepared by dissolving (50 g) of salt in (20 mL) water. Metal ion (Ni\(^{2+}\) or Co\(^{2+}\)) exchanged surfactants were prepared according to previously published methods [16, 17, 18]. Na\(^{+}\)-surfactant was dissolved in 20 mL of absolute ethanol at 1 mol dm\(^{-3}\). Saturated solution was added into (Na\(^{+}\)-surfactant) and stirred for one hour. Then, 20 mL of diethyl ether was added and shaken in a separating funnel to produce two phases. The upper diethyl ether phase contained M\(^{2+}\)-surfactant and the lower phases were removed. The upper phase was washed repeatedly with water until a colourless solution was obtained. The above process was monitored by UV-Visible Spectroscopy (Agilent).

High-Pressure Phase Behaviour of Metallosurfactants and Supercritical CO\(_2\) Viscosity Measurements

The phase behaviour of the synthesised surfactants and supercritical CO\(_2\) viscosity enhancement were examined through high-pressure cell measurement at temperatures ranging from 35 to 75 °C. A known amount of surfactants in w/scCO\(_2\) mixtures was visually observed to record the phase behaviour of the system. Observations of phase changes were examined in a high-pressure vessel with an optical window and a moving piston inside. Measurements were conducted with an invariable composition, varying the temperature and pressure of the mixture. 0.05 mol dm\(^{-3}\) surfactant and defined amount of CO\(_2\) were placed in an optical cell and equilibrated overnight with vigorous stirring at 75°C and 400 bar to obtain a transparent single phase.

A known amount of water was then introduced into the mixture via the six-port valve. The formation of a clear mixture with a water content greater than its solubility in pure scCO\(_2\) is considered to be a microemulsion. Cloud pressures (\(P_{\text{trans}}\)) were observed when the clear mixture became turbid as the pressure was adjusted and the microemulsions (1\(\Phi\)) transformed into macroemulsions (2\(\Phi\)). The amount of water dispersed in CO\(_2\) was expressed as the water-to-surfactant molar ratio (\(w\)). CO\(_2\) densities were calculated using the Span-Wagner EOS [19, 20].

RESULTS AND DISCUSSION

\(di\)-HCF\(_4\) surfactant

\(^1\)HNMR (550 MHz, CDCl\(_3\), TMS), (\(\delta_{\text{H}}/ppm\)): 3.04-3.29(a, m,2H), 4.46(b, m,1H), 4.40-4.66 (c, m,4H), 5.69-5.69(d, m,4H). Elemental Analysis: found C, 25.94; H, 1.40; S, 4.95. Calcd C, 24.24; H, 1.14; S, 4.54.

\(di\)-HCF\(_6\) surfactant

\(^1\)HNMR (550 MHz, CDCl\(_3\), TMS), (\(\delta_{\text{H}}/ppm\)): 3.29-3.04(a, m,2H), 4.46 (b,m,1H), 4.66-4.40(c, m,4H), 5.69-5.69(d, m,4H). Elemental Analysis: found C, 25.49; H, 1.07; S, 3.78. Calcd C, 23.28; H, 0.76; S, 3.15.

\(di\)-CF\(_2\) surfactant

\(^1\)HNMR (550 MHz, CDCl\(_3\), TMS), (\(\delta_{\text{H}}/ppm\)): 1.61-1.62(a, m,8H), 3.29-3.04(b, m,2H), 4.08-4.13(c, m,4H), 4.46(d, m,1H). Elemental Analysis: found C, 31.12; H, 2.80; S, 5.93. Calcd C, 30.49; H, 2.20; S, 3.69.

UV-Visible Spectroscopy

The formation of M\(^{2+}\)-surfactants was confirmed using UV-Visible spectroscopy. Surfactant formation was confirmed when no further NaNO\(_3\) and M(NO\(_3\))\(_2\) were present in the UV-visible absorbance spectra of the washings. Figures 1 – 2 show the disappearance with progressive washing (after eight washes) of the two absorbance bands in the UV-visible spectrum, at 305 nm and 394 nm, which are ascribed to the n-\(\pi^*\) transition of the nitrate ion and the d-d transition of Co\(^{3+}\) and Ni\(^{2+}\) (hexa-aqua nickel ion) [21].
High-Pressure Phase Behaviour of Metallosurfactant-CO$_2$ Systems

In order to determine the influence of surfactant structure on microemulsion phase stability, the pressure – temperature phase boundaries for the metallosurfactants di-CF$_2$, di-HCF$_4$ and di-HCF$_6$ were determined at a fixed concentration of 0.04 mol dm$^{-3}$ and various $w$ ([H$_2$O]/[surfactant]) mole ratio values. The cloud transition pressure, $P_{\text{trans}}$ was determined visually as the pressure at which the onset of cloudiness occurred on lowering the pressure at a fixed temperature. Above $P_{\text{trans}}$, the systems were transparent (1$\Phi$) and when the pressure was reduced approaching $P_{\text{trans}}$, significant cloudiness was observed (2$\Phi$).
Previously, CO\textsubscript{2}-philicity of surfactants has been achieved by fluorination of surfactant chains. For example, the maximum \( w \) loading (\( w_{\text{max}} \)) at accessible temperatures and pressures for di-CF\(_2\), di-HF\(_4\) and di-HCF\(_6\) are summarised in Table 2. The \( w_{\text{max}} \) values indicate that higher fluorine content increases the microemulsifying properties. One approach to enhance the viscosity of the uncooperative solvent CO\(_2\) is to introduce metallosurfactant by exchanging Na\(^+\) cations of a sulfosuccinate surfactant with Ni\(^{2+}\) or Co\(^{2+}\) counter ions [22]. As an initial step, the solubility of Ni(diHCF\(_4\)\(_2\) and Co(diHCF\(_4\)\(_2\) in CO\(_2\) was examined at different \( w \) ratios. The result was in agreement with earlier work by Trickett et al.[22], with uncertainties in \( P_{\text{trans}} \) no greater than 60 bar representing a realistic measure of reproducibility.

**Table 2** Phase behaviour measurements of sulfosuccinate surfactants for w/c microemulsions at 35\(^\circ\)C, \( w = 10 \) and maximum water loading (\( w_{\text{max}} \)). \(^a\)Data collected by [13]; \(^b\)Data collected by [23].

| Surfactants       | \( P_{\text{trans}} \)/ bar | \( w_{\text{max}} \) |
|-------------------|-----------------------------|---------------------|
| Co (di-CF\(_2\)\(_2\) | >400                        | 5                   |
| Co (di-HF\(_4\)\(_2\) | 267                         | 15                  |
| Co (di-HCF\(_6\)\(_2\) | 165                         | 30                  |
| Ni (di-CF\(_2\)\(_2\) | >400                        | 10                  |
| Ni (di-HF\(_4\)\(_2\) | 251                         | 25                  |
| Ni (di-HCF\(_6\)\(_2\) | 182                         | 25                  |
| di-CF\(_2\)^a     | 198                         | 20                  |
| di-HF\(_4\)^a     | 185                         | 30                  |
| di-HF\(_4\)^b     | 239                         | 35                  |
| di-HCF\(_6\)^b    | 149                         | 40                  |
| Ni (di-HCF\(_6\)\(_2\) | 185                         | 45                  |

In order to investigate the effect of fluorine content on metallosurfactants, the performance of Ni(diHCF\(_4\)\(_2\) and Co(diHCF\(_4\) was compared with the related di-CF\(_2\) and di-HCF\(_6\) surfactants. As can be seen in Figure 3, decreasing the fluorine content to di-CF\(_2\) had a significant effect on the w/c phase stability. The Ni(diCF\(_2\)\(_2\) and Co(diCF\(_2\)\(_2\) surfactants apparently result in a much lower \( w \) ratio of about \( w_{\text{max}}=5 \) and \( w_{\text{max}}=10 \) respectively, compared to the di-HF\(_4\) surfactant. Interestingly, the introduction of Ni\(^{2+}\) or Co\(^{2+}\) counter ions to the higher fluorine content di-HCF\(_6\) was shown to have a significant effect on the w/c phase stability. Co(diHCF\(_6\)\(_2\) and Ni(diHCF\(_6\)\(_2\) surfactants were able to stabilise w/c microemulsions with \( w_{\text{max}} =30 \) and \( w_{\text{max}} =25 \) respectively. From these results, it was clear that fluorination is indeed necessary to achieve the CO\(_2\)-philicity.

**Figure 3** Phase behaviour of Ni(di-HF\(_4\)\(_2\) surfactant in CO\(_2\) at various \( w \) ratios. [surfactant] = 0.04 mol dm\(^{-3}\).
Figure 4 Phase behaviour of Co(di-HCF4)₂ surfactant in CO₂ at various w ratios. [surfactant] = 0.04 mol dm⁻³

Figure 5 Phase behaviour of Co(di-CF2)₂ surfactant in CO₂ at various w ratios. [surfactant] = 0.04 mol dm⁻³

Figure 6 Phase behaviour of Ni(di-CF2)₂ surfactant in CO₂ at various w ratios. [surfactant] = 0.04 mol dm⁻³
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Figure 7 Phase behaviour of Co(di-HCF6)$_2$ surfactant in CO$_2$ at various $w$ ratios. [surfactant] = 0.04 mol dm$^{-3}$

Figure 8 Phase behaviour of Ni(di-HCF6)$_2$ surfactant in CO$_2$ at various $w$ ratios. [surfactant] = 0.04 mol dm$^{-3}$

High-Pressure Viscosity of Metallosurfactant-CO$_2$ Systems

The high-pressure relative viscosities of CO$_2$ systems as a function of different metallosurfactants are shown in Figure 9 – 10. These measurements were carried out at a surfactant concentration of 0.02 – 0.04 mol dm$^{-3}$ and in the temperature range 35 – 75 °C. The viscosity ($\eta$) data were calculated using the Hagen-Poiseuille equation (Eq. 1 – 2). Thus, the relative viscosity of the metallosurfactant-CO$_2$ systems ($\eta_{\text{mic}}/\eta_{\text{CO}_2}$) is obtained as follows:

$$\eta = \frac{\pi Pr^{4t}}{8vt}$$

$$\eta_{\text{mic}}/\eta_{\text{CO}_2} = \frac{\eta_{\text{CO}_2-\text{hybrid}}}{\eta_{\text{CO}_2}} = \frac{P_{\text{CO}_2-\text{hybrid}}}{P_{\text{CO}_2}}$$

$\eta$: Viscosity  $\eta_{\text{CO}_2}$: Viscosity of CO$_2$  $\eta_{\text{CO}_2-\text{hybrid}}$: Viscosity of compound/CO$_2$ solution  $P$: Differential pressure at the inlet and outlet of the capillary  $r$: Radius of capillary  $t$: Time  $v$: Volume of fluid  $[\eta]$: Specific viscosity  $P_{\text{CO}_2}$: Differential pressure in the pure CO$_2$ system  $P_{\text{CO}_2-\text{hybrid}}$: Differential pressure in the compound/CO$_2$ solution.

Previously, [22], using di-HCF4, showed a viscosity increase upon the introduction of nickel or cobalt salts, indicating a relationship between the chemical nature of the surfactant and the viscosity.
enhancement. The work presented here, in agreement with that study, shows that Co$^{2+}$ and Ni$^{2+}$ salts of di-HCF4 resulted in an increase in relative viscosity of up to 90%. Interestingly, increasing the $w$ ratio above $w=10$ in these di-HCF4 surfactants leads to a notable reduction in the relative viscosity. It is clear that the relative viscosity is dependent upon the mild solubility of the surfactant at lower pressures, and its ability to disperse small amounts of water [12].

Recently, efforts to reduce the proportion of fluorine atoms in the surfactant chains e.g. di-CF2 has opened up a new pathway for generating more economic CO$_2$-philic surfactants. Although the sodium version of di-CF2 has been proven to stabilise w/c microemulsions [13], here, the introduction of nickel or cobalt di-CF2 surfactant decreases the microemulsification. Of the three-fluorinated surfactants tested, di-CF2 was not able to stabilise w/c microemulsions with lower relative viscosity at lower $w$ ratios ($w < 5$). This is not surprising since weak intermolecular interactions between the fluorocarbon tails favour tail-CO$_2$ interactions and contribute to the microemulsifying capacity of fluorinated surfactants [24].

![Figure 9](image9.png) Relative viscosities of Ni(surfactant)$_2$ variants at [Surfactant] = 0.04 mol dm$^{-3}$ in CO$_2$ at 35°C.

![Figure 10](image10.png) Relative viscosities of Co(surfactant)$_2$ variants at [Surfactant] = 0.04 mol dm$^{-3}$ in CO$_2$ at 35°C.
Interestingly, Ni(diHCF6)₂ and Co(diHCF6)₂ surfactants have the highest relative viscosities. Both surfactants were able to achieve relative viscosity up to 2.10 at a temperature of 35°C. These experimental results indicate that the viscosity enhancement of scCO₂ strongly depends on the microemulsifying properties as well as the fluorine content of the surfactants [24]. The viscosity increased significantly with increasing w ratio up to w = 10. It was also observed that the relative viscosity of scCO₂ tended to decrease as the w ratio increased. In order to clearly distinguish the effect of temperature variation and surfactant concentration, the dependence of the relative viscosity of both parameters was plotted and respectively. It can be seen that the effect of temperature on the relative viscosity values was small, and the temperature varied only within a ±0.5 range. However, a decrease in the relative viscosity with increasing surfactant concentration is clearly illustrated.

Figure 11 Temperature effect on relative viscosities of di-HCF6 metallosurfactant variants at [Surfactant] = 0.04 mol dm⁻³ in CO₂ at 35 °C.

In Figures 9 – 12, all of the relative viscosities are seen to increase with increasing microemulsification capacity of the surfactant, as well as with increasing fluorine content in the surfactants. This behaviour,
noted before for w/c microemulsions, is indicative of the swelling of micelles with added water [25]. The phase behaviour is consistent with the following scenario: when micelles become swollen with water, attractive micelle-micelle interactions are strengthened, thus higher pressures are required to overcome tail/tail interactions and prevent phase separation. Comparison of the relative viscosity performance with other surfactants as shown in Figure 13 indicate limited water uptake in reverse micelles by the lower fluorine content surfactants. Nevertheless, Ni(di-HCF6)2 and Co(di-HCF6)2 in particular, clearly outperform most other surfactants, exhibiting the highest relative viscosities and allowing stable microemulsion formation. For comparison purposes, lower relative viscosity values have been reported for costly hybrid sulfate surfactants e.g. K-F7H4 [26], the maximum w value being 30.

![Figure 13 Relationship of maximum relative viscosity with fluorine content of surfactants](image)

**CONCLUSIONS**

In this paper, a systematic study was made of metallosurfactant (nickel (Ni2+) or cobalt (Co2+) counterion) sulfosuccinate surfactants, thus offering an acceptable solution for carbon dioxide viscosity modification in enhanced oil recovery applications. Metallosurfactants were successfully synthesised using three different double chain, fluorinated sulfosuccinate surfactants, namely sodium bis (4H, 4H, 5H, 5H-pentafluoropentyl)-2-sulfosuccinate (di-CF2), sodium bis (1H, 1H, 5H-perfluoropentyl)-2-sulfosuccinate (di-HCF4) and sodium bis (1H, 1H, 7H-perfluorohexyl)-2-sulfosuccinate (di-HCF6) according to well-documented preparation methods. The surfactant purity (both on the organic and physico-chemical levels) was confirmed by 1H nuclear magnetic resonance, UV-visible spectroscopy and also by elemental analysis (EA). Among these surfactants, the metallosurfactants utilising sodium bis (1H, 1H, 7H-perfluorohexyl)-2-sulfosuccinate (di-HCF6) were the only ones that were able to stabilise w/c microemulsions via the formation of reverse micelles at lower cloud point pressures ($P_{trans}$). Interestingly, increasing the fluorine content of di-HCF6 metallosurfactant showed significance increases in the relative viscosity of CO$_2$. di-HCF6 metallosurfactant were able to achieve relative viscosities up to 2.10 at a temperature of 35°C. Although the sodium version of di-CF2 has been proven to stabilise w/c microemulsions, of the three-fluorinated surfactants tested, di-CF2 metallosurfactants were not able to stabilise w/c microemulsions with lower relative viscosity at lower w ratios (w < 5). This observation is not surprising since weak intermolecular interactions between the fluorocarbon tails favour tail-CO$_2$ interactions and contribute to the strongly microemulsifying properties of the fluorinated metallosurfactants. In summary, this work has advanced the understanding of how surfactants can be used to modify the physical properties of liquid carbon dioxide. In particular, it was shown that control
over solvent viscosity can be achieved using the principles of molecular self-assembly with custom-made CO$_2$ compatible surfactants.

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