Alqalam Journal of Medical and Applied Sciences. 2025;8(2):1209-1218
https://doi.org/10.54361/ajmas.2582102

Original article

Carbon Dioxide Viscosity Modifier for Enhanced Oil Recovery EOR Application

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Abstract
This study focuses on a new approach to enhance the viscosity of supercritical CO2 (scCO2) for enhanced oil recovery EOR applications. Fluorinated surfactants have been synthesised and used as viscosity modifiers; however, there is no systematic studies have been carried out toward scCO2 viscosity enhancement, thus impeding the commercial developments. Here, metallosurfactant structure design was focused on anionic surfactant analogues of Aerosol -OT (sodium bis (2-ethylhexyl) sulfosuccinate). The metallosurfactants were synthesised with modification on the surfactant chain with the introduction of nickel (Ni2+) and manganese (Co2+) counter ions. Nuclear Magnetic Resonance (NMR) Spectroscopy, Elemental analysis (EA), UV-Visible Spectroscopy and High-Pressure Viscometer have investigated the metallosurfactant. The result shows that fluorination is a crucial factor influencing Aerosol-OT surfactant analogue compatibility with scCO2. The presence of fluorine in the metallosurfactant chemical structure gives rise to relative scCO2 viscosity. The results obtained are beneficial for CO2 studies in enhanced oil recovery applications.

Keywords: Enhanced Oil Recovery EOR, Carbon Dioxide, supercritical CO2(scCO2), Surfactant.

Introduction

The carbon dioxide at reservoir conditions is less dense than water and may be more or less dense than the crude oil and 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 °C and P_c = 73 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]. In contrast, many other common solvents either have much higher critical temperatures/pressures e.g., water (T_c = 374 °C and P_c = 221 bar), toluene (T_c = 319 °C and P_c = 41 bar); or are flammable (and therefore regulated) e.g., ethane with T_c = 32 °C and P_c = 49 bar [2]. 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 [3] 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 [4]. 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 [5]; 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].

Two important oil and gas industry processes that use supercritical carbon dioxide ($scCO_2$) are fracture stimulation and enhanced oil recovery. Although the problems with using $scCO_2$ have been well studied and documented in laboratory and field studies, the low viscosity of $scCO_2$ causes it to 'finger' towards production wells and bypass large amounts of oil [8]. Significant research has been conducted over the past 30 years searching for ways to increase the viscosity of carbon dioxide. Because of its low viscosity, the effectiveness of $scCO_2$ as a fracturing fluid has been questioned. Specifically, the effect of low fluid viscosity on proppant settling, the placement of high sand concentration, and fluid leak-off is poorly understood. Considering the huge difference in viscosity between $scCO_2$ and gelled fluids, an increase in the viscosity of carbon dioxide could improve the placement of sand particles of greater size and in greater numbers and improve fluid leak-off. Research focussed on the area of carbon dioxide viscosity enhancement is therefore important in order to improve the efficiency of CO_2-sand fracturing. Most research efforts to date have aimed to increase the viscosity of dense carbon dioxide via the dissolution of dilute concentrations (less than 1 wt. %) of 'thickeners' [9].

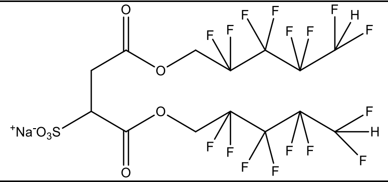
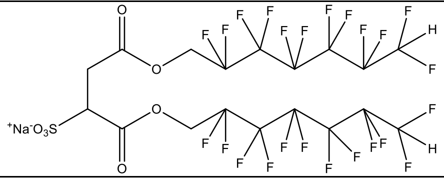
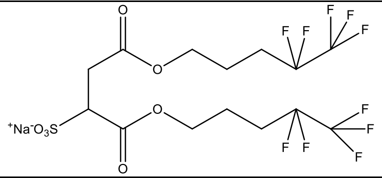
Recently extremely high molecular weight polymers have been tested in $scCO_2$ [10]. These compounds were either insoluble or sparingly soluble in carbon dioxide unless prohibitive amounts of co-solvent were added. Using a different strategy, relatively low molecular weight compounds capable of forming viscosity-enhancing pseudo-networks of polymers via associations, hydrogen-bonding, or micelle formation were evaluated [11]. These compounds contain polar groups that reduce their solubility in carbon dioxide. Hence, large amounts of co-solvent were required to enhance their CO_2 solubility in order to increase the viscosity. Another recent approach has been to design novel viscosity enhancing molecules that exhibit very high carbon dioxide solubility. One high-molecular weight (MW) CO_2-thickening polymer, a polyfluoroacrylate;

***Received**: 26-04-2025 - **Accepted**: 19-06-2025 - **Published**: 29-06-2025*

and one low MW associative thickener, a fluoroether disulphate telechelic ionomer have been identified [12-13]. Both can increase the viscosity of carbon dioxide in concentrations of several weight percent without the need for a co-solvent, but they are synthesised using expensive, highly fluorinated precursors.

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 [14]. 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 fluorine content surfactants have been identified that can stabilise water-in-CO_2 (w/c) microemulsions [15-16]. Interestingly, this is the first time that these transition metal counterions have been incorporated into low fluorine CO_2-philic surfactants or recognised as metallosurfactants and systematically studied in $scCO_2$. Thus, the introduction of transition metal counterions to low fluorine 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 EOR applications.

Table 1. Double-chain fluorinated sulphosuccinate surfactants used in this study

Surfactant	**Surfactant structure**	**Chemical Name**
di-HCF4		Sodium bis (*1H, 1H, 5H*-perfluoropentyl)-2-sulphosuccinate
di-HCF6		Sodium bis (*1H*, 1H, 7H-perfluoroheptyl)-2-sulphosuccinate.
di-CF2		Sodium bis (*4H, 4H, 5H, 5H, 5H*-pentafluoropentyl)-2-sulphosuccinate.

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-sulphonic acid monohydrate 98% (Merck), sodium hydrogen sulphite (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), 1,2-dioxane 99% (Systerm), acetone 99.5% (Systerm), ethanol 99% (Systerm), diethyl ether 99% (Systerm). CO_2 99.99% purity (Nippon Ekitan Co., Ltd.) was used without further treatment.

Surfactant Synthesis

Synthesis of Double-chain Fluorinated Sulphosuccinate Surfactants

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

Esterification

A mixture of alcohol (2.2 eq), maleic anhydride (1.0 eq), p-toluene-4-sulphonic 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 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-sulphonic acid monohydrate (0.2 eq). Solvent was removed using a rotary evaporator and the diester was obtained as a yellow liquid.

***Received**: 26-04-2025 - **Accepted**: 19-06-2025 - **Published**: 29-06-2025*

Purification of Diester (Column Chromatography)

Column chromatography was prepared by using silica powder (SiO_2) 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), 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.

Sulphonation

The diester was first dissolved using 1-2 dioxane for the fluorinated diesters, and water was added to the mixture until saturation. Sodium hydrogen sulphite (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 dissolved 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.

Preparation of Metal (Ni^{2+} or Co^{2+}) Exchanged Surfactants (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 (Ni^{2+} or Co^{2+}) exchanged surfactants were prepared according to previously published methods [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.

High-Pressure Phase Behaviour of Surfactants 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 number 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_{trans}) were observed when the clear mixture became turbid as the pressure was adjusted and the microemulsions (1Φ) transformed into macroemulsions (2Φ). 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].

Results and discussion

Fluorinated/di-HCF4

^{1}HNMR (550 MHZ, CDCl3, TMS), (δ_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.

Fluorinated/di-HCF6

^{1}HNMR (550 MHz, $CDCl_3$, TMS), (δ_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.

Fluorinated/di-HF2

^{1}HNMR (550 MHZ, CDCl3, TMS), (δ_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

***Received**: 26-04-2025 - **Accepted**: 19-06-2025 - **Published**: 29-06-2025*

absorbance bands in the UV-visible spectrum, at 305 nm and 394 nm, which are ascribed to the n-π* transition of the nitrate ion and the d-d transition of Co^{2+} and Ni^{2+} (hexa-aqua nickel ion[20].

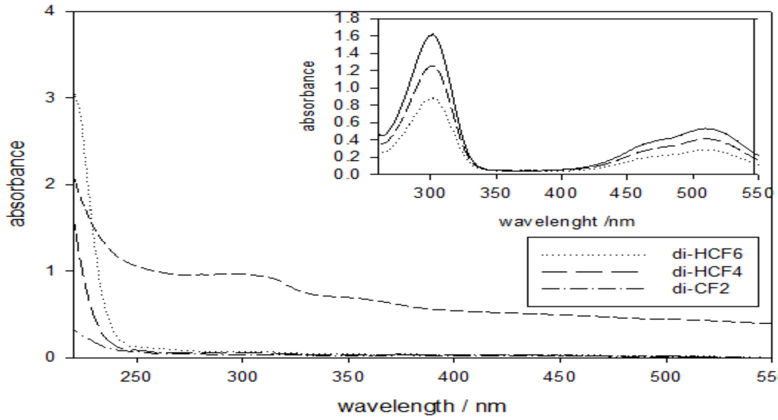


Figure 1. UV-visible absorbance spectra of the aqueous washings used to remove $NaNO_3$ and $Co(NO_3)_2$ impurities from M^{2+}-surfactants. Inset: spectra before the washing process.

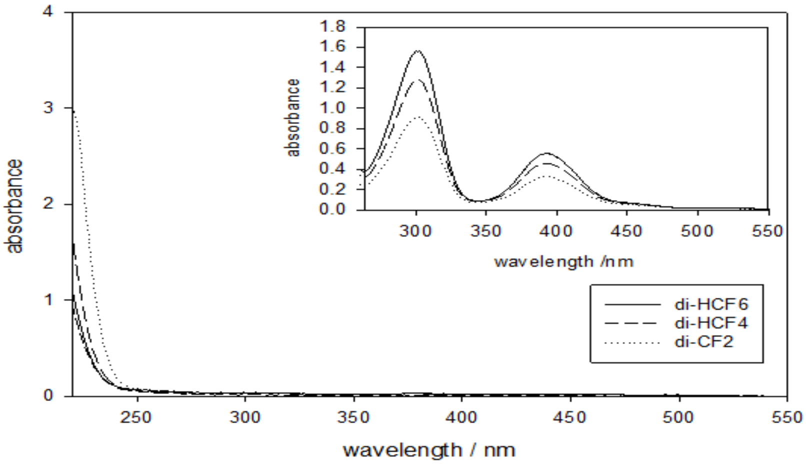


Figure 2. UV-visible absorbance spectra of the aqueous washings used to remove $NaNO_3$ and $Ni(NO_3)_2$ impurities from M^{2+}-surfactants. Inset: spectra before the washing process.

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-CF2, di-HCF4 and di-HCF6 were determined at a fixed concentration of 0.04 mol dm^{-3} and various w ($[H_2O]/[surfactant]$) mole ratio values. The cloud transition pressure, P_{trans} was determined visually as the pressure at which the onset of cloudiness occurred on lowering the pressure at a fixed temperature. Above P_{trans}, the systems were transparent (1Φ) and when the pressure was reduced approaching P_{trans}, significant cloudiness was observed (2Φ).

Previously, CO_2-philicity of surfactants has been achieved by fluorination of surfactant chains. For example, the maximum w loading (w_{max}) at accessible temperatures and pressures for di-CF2, di-HF4 and di-HCF6 are summarised in Table 2. The w_{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 sulphosuccinate surfactant with Ni^{2+} or Co^{2+} counter ions [21]. As an initial step, the solubility of $Ni(diHCF4)_2$ and $Co(diHCF4)_2$ in CO_2 was examined at different at w ratios The result was in agreement with earlier work by Trickett et al., with uncertainties in P_{trans} no greater than 60 bar representing a realistic measure of reproducibility.

Table 2. Phase behaviour measurements of sulphosuccinate surfactants for w/c microemulsions at 35°C, w = 10 and maximum water loading (w_{max}). ^{a}Data collected by Mohamed et al. ^{b}Data collected by Eastoe et al.

Surfactants	P_{trans} / bar	w_{max}
Co (di-CF2)$_2$	>400	5
Co (di-HCF4)$_2$	267	15
Co (di-HCF6)$_2$	165	30
Ni (di-CF2)$_2$	>400	10
Ni (di-HCF4)$_2$	251	25
Ni (di-HCF6)$_2$	182	25
di-CF2^a	198	20
di-HCF4^a	185	30
di-HCF4^b	239	35
di-HCF6	149	40
di-HCF6^b	185	45

In order to investigate the effect of fluorine content on metallosurfactants, the performance of Ni(diHCF4)$_2$ and Co(diHCF4) was compared with the related di-CF2 and di-HCF6 surfactants. As can be seen in Figure 3 – 8, decreasing the fluorine content to diCF2 had a significant effect on the w/c phase stability. The Ni(diCF2)$_2$ and Co(diCF2)$_2$ surfactants apparently result in a much lower w ratio of about w_{max}=5 and w_{max} =10 respectively, compared to the di-HCF4 surfactant. Interestingly, the introduction of Ni^{2+} or Co^{2+} counter ions to the higher fluorine content di-HCF6 was shown to have a significant effect on the w/c phase stability. Co(diHCF6)$_2$ and Ni(diHCF6)$_2$ surfactants were able to stabilise w/c microemulsions with w_{max} =30 and w_{max} =25 respectively. From these results, it was clear that fluorination is indeed necessary to achieve the CO$_2$-philicity.

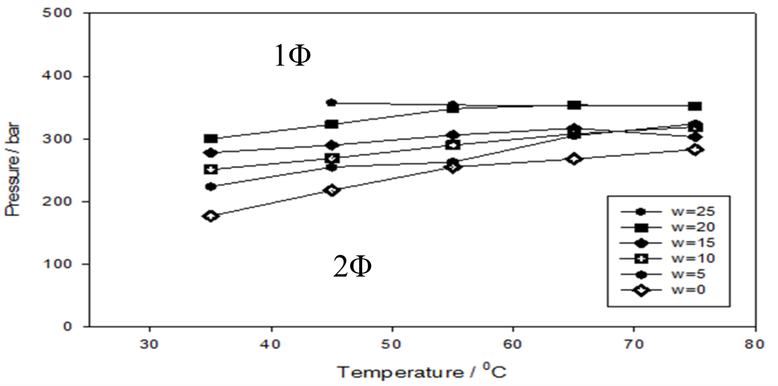


Figure 3. Phase behaviour of Ni(di-HCF4)$_2$ surfactant in CO$_2$ at various w ratios. [surfactant] = 0.04 mol dm^{-3}

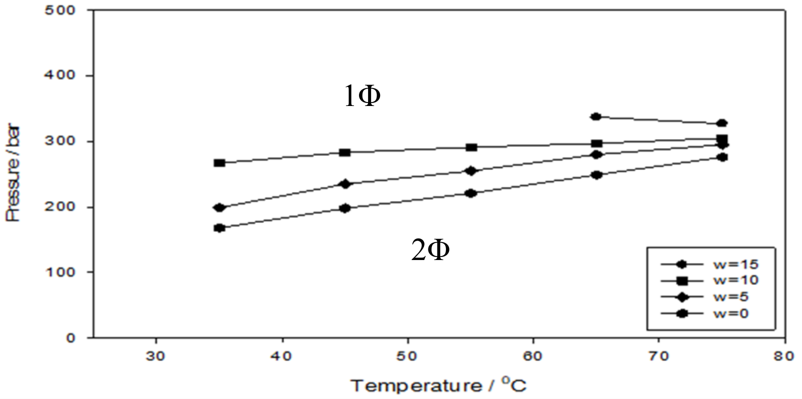


Figure 4. Phase behaviour of Co(di-HCF4)$_2$ surfactant in CO$_2$ at various w ratios. [surfactant] = 0.04 mol dm^{-3}

***Received**: 26-04-2025 - **Accepted**: 19-06-2025 - **Published**: 29-06-2025*

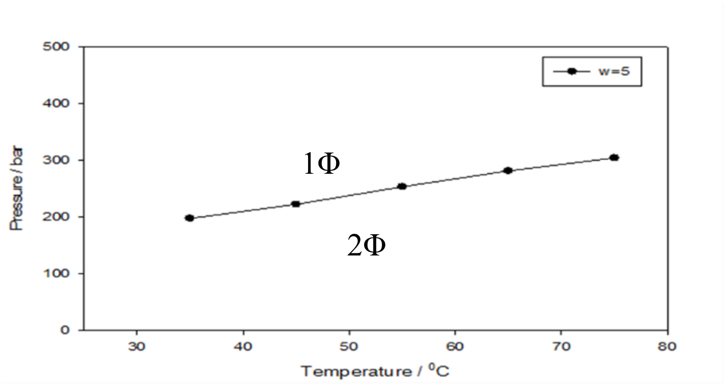


Figure 5. Phase behaviour of Co(di-CF2)₂ surfactant in CO₂ at various w ratios. [surfactant] = 0.04 mol dm⁻³

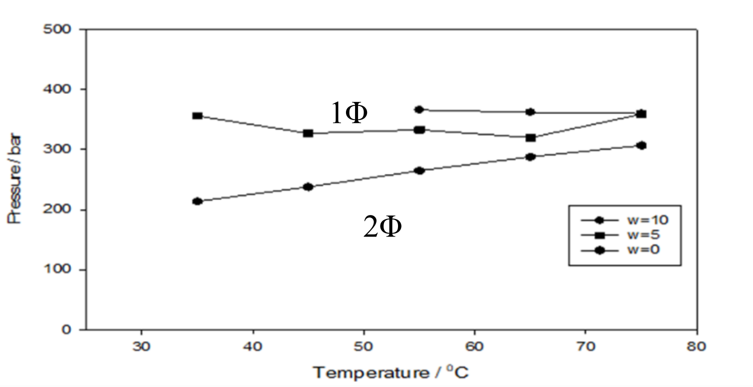


Figure 6. Phase behaviour of Ni(di-CF2)₂ surfactant in CO₂ at various w ratios. [surfactant] = 0.04 mol dm⁻³

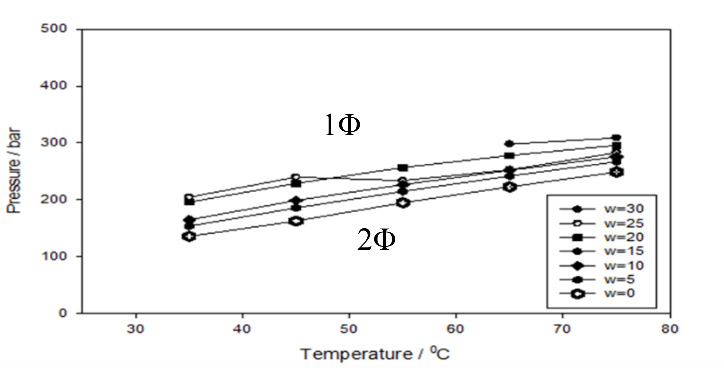


Figure 7. Phase behaviour of Co(di-HCF6)₂ surfactant in CO₂ at various w ratios. [surfactant] = 0.04 mol dm⁻³

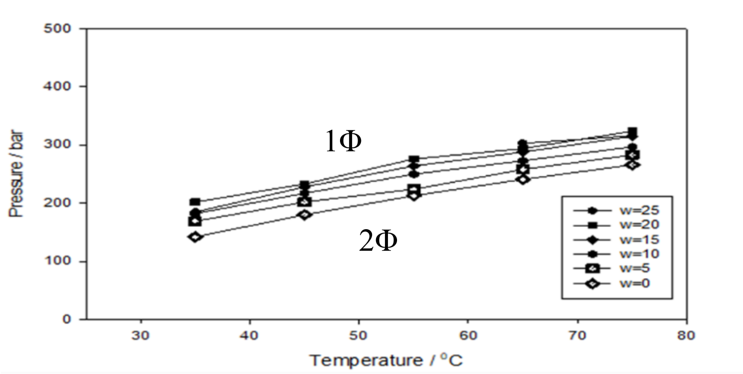


Figure 8 Phase behaviour of Ni(di-HCF6)₂ surfactant in CO₂ at various w ratios. [surfactant] = 0.04 mol dm⁻³

High-Pressure Viscosity of Metallosurfactant-CO₂ 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

Received: *26-04-2025* - ***Accepted***: *19-06-2025* - ***Published***: *29-06-2025*

dm^{-3} and in the temperature range 35 – 75 °C. The viscosity (η) data were calculated using the Hagen-Poiseuille equation (Eq. 1 – 2). Thus, the relative viscosity of the metallosurfactant-CO_2 systems (η mic/ η CO_2) is obtained as follows:

$$\eta = \frac{\pi P r^4 t}{8 v l} \qquad (1)$$

$$\eta_{mic}/\eta_{CO2} = \frac{\eta_{CO_2-hybrid}}{\eta_{CO_2}} = \frac{P_{CO_2-hybrid}}{P_{CO_2}} \qquad (2)$$

$\boldsymbol{\eta}$: Viscosity $\boldsymbol{\eta_{CO_2}}$: Viscosity of CO_2 $\boldsymbol{\eta_{CO_2-hybrid}}$: 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 **[η]** : Specific viscosity $\boldsymbol{P_{CO_2}}$: Differential pressure in the pure CO_2 system $\boldsymbol{P_{CO_2-hybrid}}$: 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 [23].
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 [24], 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 [25].

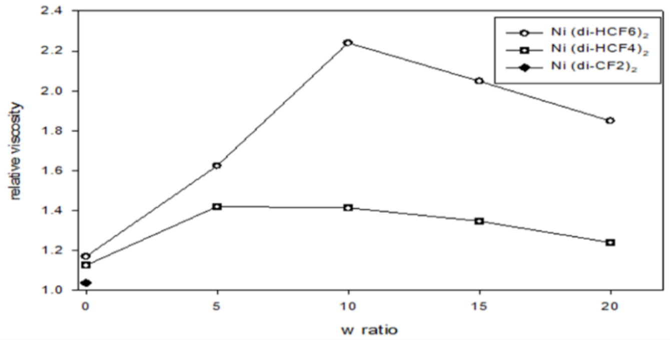


Figure 9. Relative viscosities of Ni(surfactant)$_2$ variants at [Surfactant] = 0.04 mol dm^{-3} in $scCO_2$ at 35°C.

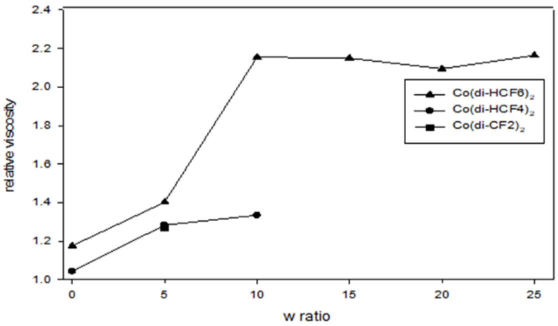


Figure 10. Relative viscosities of Co(surfactant)$_2$ variants at [Surfactant] = 0.04 mol dm^{-3} in $scCO_2$ at 35°C.

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 $scCO_2$ strongly depends on the microemulsifying properties as well as the fluorine content of the surfactants. The viscosity increased significantly with increasing *w* ratio up to *w* = 10. It was also observed that the relative viscosity of $scCO_2$ 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 separately. It can be seen that the effect of temperature on the relative viscosity values was small, and the temperature varied

***Received**: 26-04-2025 - **Accepted**: 19-06-2025 - **Published**: 29-06-2025*

only within a ±0.5 range. However, a decrease in the relative viscosity with increasing surfactant concentration is clearly illustrated.

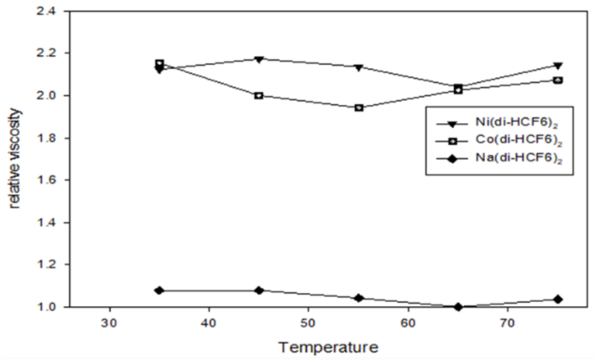


Figure 11. Temperature effect on relative viscosities of di-HCF6 metallosurfactant variants at [Surfactant] = 0.04 mol dm^{-3} in scCO$_2$ at 35 °C.

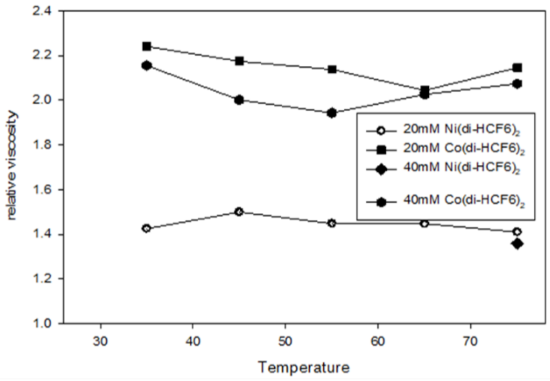


Figure 12 Temperature effect on relative viscosities of di-HCF6 metallosurfactant variants at different [Surfactant] in scCO$_2$ at 35 °C.

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 [26]. 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 sulphate surfactants e.g., K-F7H4, the maximum w value being 30.

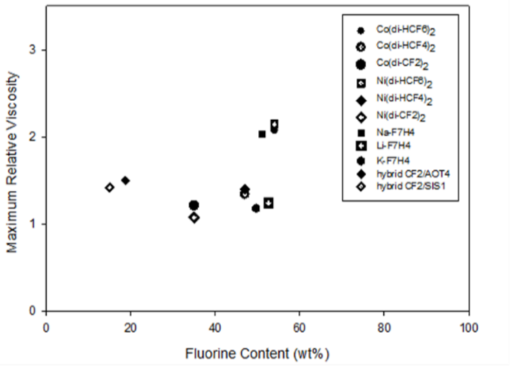


Figure 13. Relationship of maximum relative viscosity with fluorine content of surfactants

Conclusion

In this study, a systematic study was made of metallosurfactant (nickel (Ni^{2+}) or cobalt (Co^{2+}) counterion) sulphosuccinate surfactants, thus offering an acceptable solution for carbon dioxide viscosity modification

***Received**: 26-04-2025 - **Accepted**: 19-06-2025 - **Published**: 29-06-2025*

in enhanced oil recovery EOR applications. Metallosurfactants were successfully synthesised using three different double chain, fluorinated sulphosuccinate surfactants, namely sodium bis (*4H, 4H, 5H, 5H, 5H*-pentafluoropentyl)-2-sulphosuccinate (di-CF2), sodium bis (*1H, 1H, 5H*-perfluoropentyl)-2-sulphosuccinate (di-HCF4) and sodium bis (*1H, 1H, 7H*-perfluoroheptyl)-2-sulphosuccinate (di-HCF6) according to well-documented preparation methods. The surfactant purity (both on the organic and physico-chemical levels) was confirmed by ^{1}H nuclear magnetic resonance, UV-visible spectroscopy and also by elemental analysis (EA). Among these surfactants, the metallosurfactants utilising sodium bis (1H, 1H, 7H-perfluoroheptyl)-2-sulphosuccinate (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 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.

Conflict of interest. Nil

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***Received**: 26-04-2025 - **Accepted**: 19-06-2025 - **Published**: 29-06-2025*

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Received*: 26-04-2025 -* ***Accepted****: 19-06-2025 -* ***Published****: 29-06-2025*