

INCREASING THE VISCOSITY OF CO₂ WITH SURFACTANTS TO IMPROVE EOR PERFORMANCE

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ABSTRACT

1.5 billion Standard cubic feet of CO₂ are injected into US oilfields each day, resulting in the recovery of about 200,000 barrels of oil. The low viscosity of CO₂ results in viscous fingering and poor volumetric sweep efficiency. If the viscosity of dense CO₂ could be increased by a factor of 2-20, much less CO₂ would be required to recover the oil. It is possible to increase the viscosity (thicken) dense, high pressure CO₂ via the self assembly of CO₂-soluble surfactants which are able to form rodlike micelles. Three semi-fluorinated surfactants have been synthesized in order to test this concept; one with a monovalent cation and a single twin-tail, Na⁺((COOCH₂C₄F₈H)₂CH₂CHSO₃)⁻¹ or Na(di-HCF₄), and two with a divalent cation and two twin-tails, Ni⁺²((COOCH₂C₄F₈H)₂CH₂CHSO₃)⁻¹)₂ or Ni(di-HCF₄)₂ and Co⁺²((COOCH₂C₄F₈H)₂CH₂CHSO₃)⁻¹)₂ or Co(di-HCF₄)₂. The fluorinated groups are highly CO₂-philic and therefore increase the solubility of these surfactants in CO₂, while the cationic metal groups are CO₂-phobic, consequently leading to the intermolecular interactions that increasing the CO₂ viscosity. Phase behavior results indicate that all three surfactants are soluble to at least 5wt% in CO₂ at 295K and pressures less than 20 MPa. SANS results indicate that only the surfactants with divalent metal ions and two twin tails form cylindrical micelles in CO₂. Falling cylinder viscometry results show that between shear rates of 6000 – 11000 s⁻¹, enhancements in viscosity compared to pure CO₂ of 20 – 90% were attained using 6 – 10wt% of either the Co(di-HCF₄)₂ or Ni(di-HCF₄)₂.

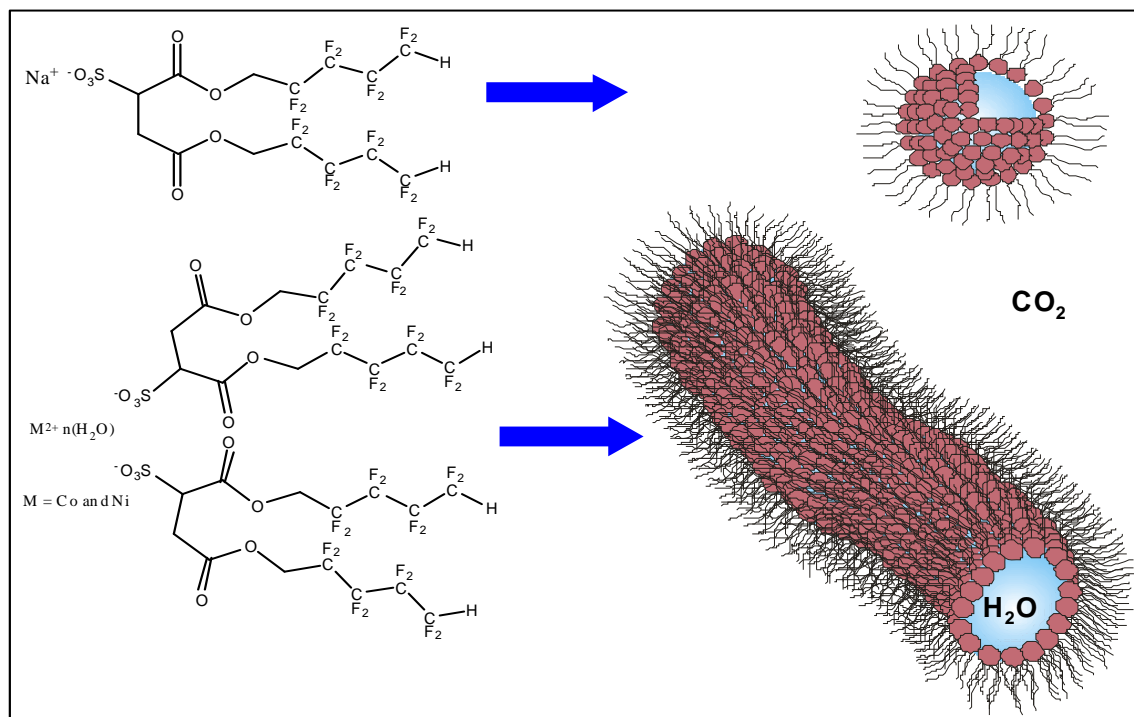


Figure 1: Structures of $\text{Na}(\text{di-HCF}_4)$ and $\text{M}^{2+}(\text{di-HCF}_4)_2$

INTRODUCTION

One successful commercial application of CO_2 is enhanced oil recovery (CO_2 -EOR). However, the efficiency of this process is severely hindered by the low viscosity of CO_2 which promotes fingering of the CO_2 through the oil rather than the desired displacement of entrapped oil. In comparison to aqueous media or hydrocarbon oils, the ability to enhance the viscosity of this weak and uncooperative CO_2 solvent is very limited. Although dense CO_2 is a reasonably strong solvent for light hydrocarbons in crude oil, it is generally only a feeble solvent for higher molecular weight compounds, such as potential thickening agents. As such, this problem of low solubility is especially acute for thickeners bearing polar or ionic groups, which are needed to efficiently promote viscosity-enhancing strong intermolecular associations. Therefore, viscosity modifiers commonly used in oily solvents are totally incompatible with, and insoluble in, CO_2

An effective way to promote viscosity enhancements is to add surfactants, which self-assemble to form thread-like, or rod-like micelles. A broad range of surfactants are known for generating viscous, visco-elastic and gel-like phases of both aqueous and organic media. However, none of the known surfactants demonstrate any appreciable CO_2 solubility, or any tendency to form reversed cylindrical micelles in this unusual solvent. Although to date there have been no reports of rod-like micelle formation in dense CO_2 , there are limited literature examples of surfactant-induced viscosity enhancements in low density hydrocarbons, including the use of lecithin in near-critical propylene and hydroxyaluminum di(2-ethyl hexanoate) in liquid propane.

Solutions and reversed micelles of fluorinated Na^+ , Co^{2+} , Ni^{2+} surfactants in CO_2 have been investigated by high pressure phase behavior, small-angle neutron scattering (HP-SANS) and viscosity experiments. The results show that stable solutions in pressurized CO_2 occur with all three surfactants, and importantly with the Ni^{2+} and Co^{2+} systems long, thin reversed micellar rods are formed, which at 6 – 10 wt% can lead to viscosity enhancements of 20 – 90% compared to pure CO_2 . This paper describes the first examples of CO_2 viscosity modifiers based on anisotropic reversed micelles, which may have important ramifications for the design of new thickeners to enhance the efficiency of processes such as CO_2 -EOR.

EXPERIMENTAL

Surfactants

Synthesis, purification and chemical characterization of the fluorinated surfactant $\text{Na}(\text{di-HCF}_4)$ have been fully described elsewhere [1]. $\text{M}^{2+}(\text{di-HCF}_4)$ analogues were prepared from the sodium salt using a liquid-liquid ion exchange process, which has also been described previously [2]. All surfactants were solids at room temperature and pressure.

Phase Behavior

A pre-weighed amount of surfactant was added to a pressure cell, followed by an aliquot of water to give the desired water/surfactant ratio, which is defined as $w = [\text{water}]/[\text{surfactant anion}]$. Note, in order to compare monovalent and divalent salts, the w value was defined with respect to surfactant anion concentration. The phase behavior studies of our CO_2 thickeners are performed at room temperature, using a high pressure, variable-volume, windowed cell, a quartz tube with a floating piston, and an o-ring in the middle of the piston is used to separate the sample volume on the top and overburden silicon oil on the bottom. The system is rated to 10000psi and 180°C. The cloud point pressure is the minimum pressure required to keep the thickener dissolved in CO_2 . Below this pressure, the solution becomes a two-phase system.

High-Pressure Viscometry

High-pressure falling-cylinder viscometry was conducted with the same pressure cell used for phase behavior experiments. An aluminum cylinder, with a diameter slightly less than the inside dimension of the hollow quartz tube, was placed in the cell along with surfactant and water. After introduction of CO_2 and attainment of single-phase conditions, the entire cell was rapidly inverted. The terminal velocity of the free falling cylinder was then measured. The shear rates, as determined from an analytical solution of the Navier Stokes equation, were between 6000 – 11000 s^{-1} . The relative viscosity increase $\eta_{\text{mic}}/\eta_{\text{CO}_2}$ is then the ratio of cylinder terminal velocity in the surfactant solution compared to that for neat CO_2 , at the same temperature and pressure. (Owing to limited quantities of the surfactants it was not possible to explore the non-Newtonian characteristics using cylinders of varying diameter.)

RESULTS AND DISCUSSION

Phase Behavior

The effect of surfactant concentration and w on the stability of $\text{Co}(\text{di-HCF}_4)_2$ surfactant in CO_2 was established (Figure 2). The system was further expanded until a bubble of CO_2 was observed in the presence of the two liquid phases; this pressure is denoted as the LLV three-phase pressure. Three values of w were selected; 0, 10 and 15, and results are shown in Figure 2. As expected, the pressure required to dissolve the surfactant increased with concentration. Further, the cloud point locus shifts to markedly higher pressures on increasing w , reflecting the additional CO_2 solvent strength required to solubilize micelles swollen with increasing amounts of water. For a certain formulation (marked x in figure 2) repeat phase measurements were conducted, with the same batch of surfactant, in different cells (one in Pittsburgh USA, the other Bristol UK) and by different operators. These repeats indicate uncertainties in cloud point pressure of typically 20 bar, but no greater than 50 bar, representing a realistic measure of the reproducibilities. Similar trends in cloud point pressure for both surfactant concentration and w were also evident for $\text{Ni}(\text{di-HCF}_4)_2$.

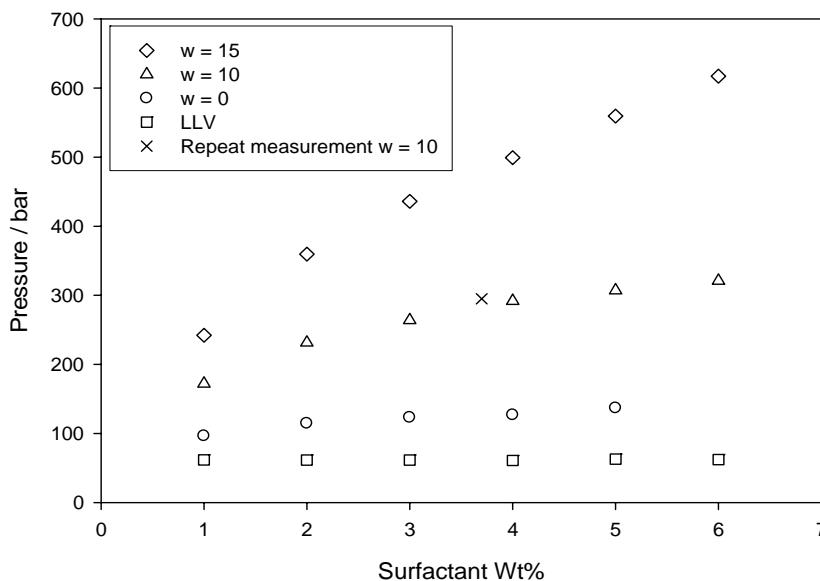


Figure 2: Phase diagram comparing effect of surfactant concentration and w on the stability of $\text{Co}(\text{di-HCF}_4)_2$ surfactant in CO_2 . Point marked x represents repeat phase measurement conducted, with the same batch of surfactant but in a different cell and by a different operator.

In addition, $\text{Ni}(\text{di-HCF}_4)_2$ phase behavior was also investigated, similar results has been achieved (Figure.3).

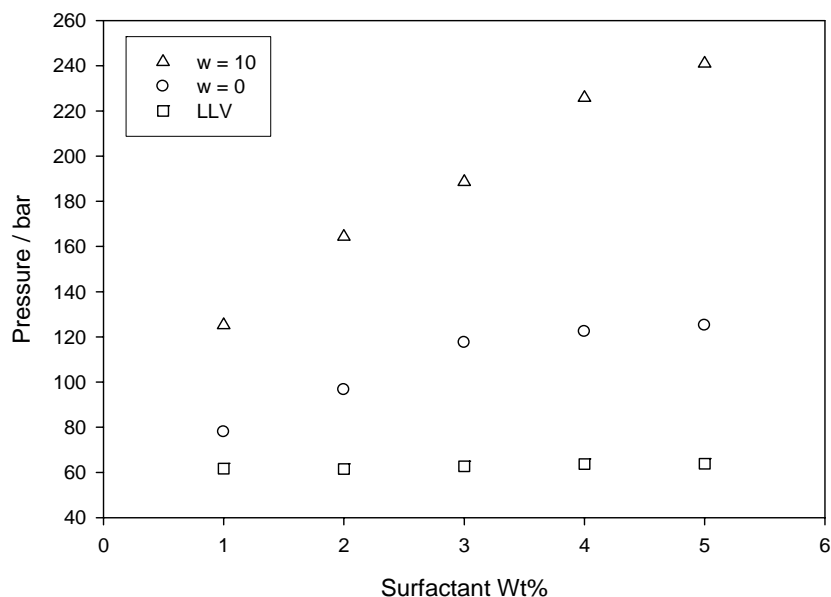


Figure 3: Phase diagram comparing effect of surfactant concentration and w on the stability of $\text{Ni}(\text{di-HCF4})_2$ surfactant in CO_2 .

Viscosity Enhancements in CO_2

High-pressure viscosity measurements at 25 °C and 350 bar are reported in terms of $\eta_{\text{mic}}/\eta_{\text{CO}_2}$, the ratio of micellar solution viscosity (η_{mic}) compared to that for neat CO_2 (η_{CO_2}). With $\text{Na}(\text{di-HCF4})$ only modest viscosity enhancements were noted: for example at 6 wt% $\eta_{\text{mic}}/\eta_{\text{CO}_2}$ was 1.15, signifying merely a 15% increase in viscosity over the background CO_2 solvent. This is because dilute spherical micelles formed by $\text{Na}(\text{di-HCF4})$ should result in only minimal effects on the solution viscosity η_{mic} .

On the other hand, as shown in Figure 4 for the rod micelle forming $\text{Ni}(\text{di-HCF4})_2$, a distinct viscosity increase was observed at 6 wt% with $\eta_{\text{mic}}/\eta_{\text{CO}_2} \sim 1.4$ (~ 40% greater than CO_2 solvent). As surfactant concentration was increased up to 10 wt% the ratio $\eta_{\text{mic}}/\eta_{\text{CO}_2}$ nearly doubles. Viscosities for the $\text{Co}(\text{di-HCF4})_2$ surfactant were also determined, albeit over a limited concentration range (Figure 4). Again, as for the Ni^{2+} derivative this Co^{2+} surfactant exerts a greater effect on viscosity compared to the Na^+ relative, and $\eta_{\text{mic}}/\eta_{\text{CO}_2} \sim 1.2$ at 6 wt%, raising to 1.6 (i.e. 60%) at 7wt% of $\text{Co}(\text{di-HCF4})_2$.

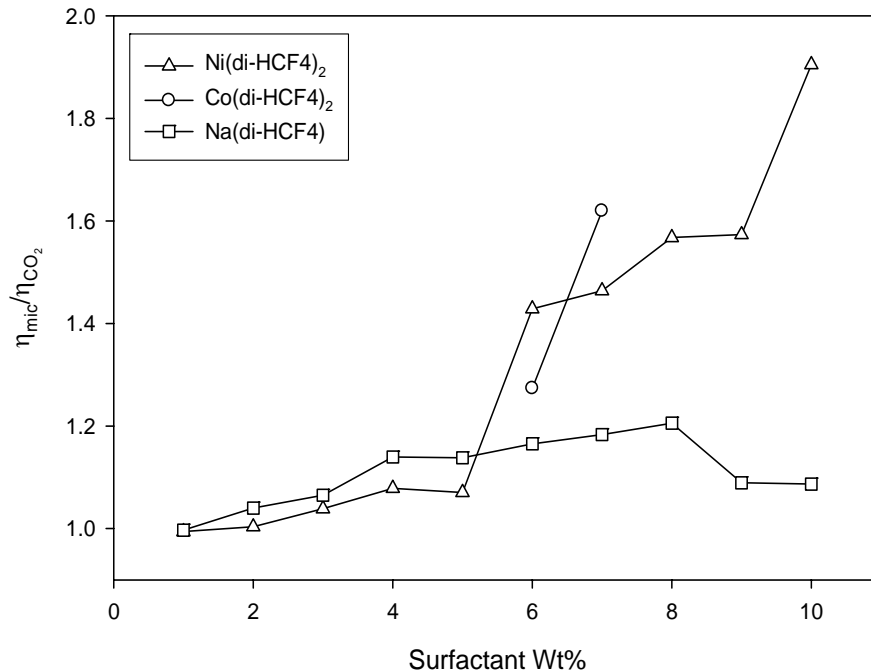


Figure 4: High-pressure viscosity measurements at 25°C and 350 bar showing the effect of surfactant counterion on relative viscosity η_{mic}/η_{CO_2} , the ratio of micellar solution viscosity (η_{mic}) compared to that for neat CO₂ (η_{CO_2}).

CONCLUSION

The fluorinated Na⁺, Co²⁺, Ni²⁺ surfactants have excellent solubility in CO₂, and viscosity increases of 20 – 90% over shear rates 6000 – 11000 s⁻¹ were attained using 6 – 10 wt% of either the Co(di-HCF4)₂ and Ni(di-HCF4)₂ surfactants. In contrast, the spherical micelle-forming Na(di-HCF4) surfactant resulted in only minor viscosity increases of ~10% at concentrations up to 10 wt%, which demonstrates the spherical micelles formed by fluorinated Na⁺ surfactant has much less contribution to the CO₂ viscosity enhancement, compared to those of cylindrical micelles formed by fluorinated Co²⁺, Ni²⁺ surfactants.

Reference

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