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ACCEPTED MANUSCRIPT

Carbon Dioxide-in-Oil Emulsions Stabilized with Silicone-Alkyl Surfactants for Waterless Hydraulic Fracturing

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Keywords

Waterless emulsions, carbon dioxide in oil emulsions, carbon dioxide – oil interface, emulsion stability, silicone, PDMS, non-fluorous, comb polymers.

Abstract

The design of surfactants for CO₂/oil emulsions has been elusive given the low CO₂-oil interfacial tension, and consequently, low driving force for surfactant adsorption. Our hypothesis is that waterless, high pressure CO₂/oil emulsions can be stabilized by hydrophobic comb polymer surfactants that adsorb at the interface and sterically stabilize the CO₂ droplets. The emulsions were formed by mixing with an impeller or by co-injecting CO₂ and oil through a beadpack (CO₂ volume fractions (ϕ) of 0.50 to 0.90). Emulsions were generated with comb polymer surfactants with a polydimethylsiloxane (PDMS) backbone and pendant linear alkyl chains. The C₃₀ alkyl chains are CO₂-philic but only partially oleophilic. The adsorbed surfactants sterically stabilized CO₂ droplets against Ostwald ripening and coalescence. The optimum surfactant adsorption was obtained with a PDMS degree of polymerization of ~88 and seven C₃₀ side chains. The emulsion apparent viscosity reached 18 cP at a ϕ of 0.70, several orders of magnitude higher than the viscosity of pure CO₂, with CO₂ droplets in the 10 – 150 µm range. These

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