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The CO_2-Solubility and Viscosity Enhancing Potential of Self-Associating CO_2-Philes

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The low viscosity of CO_2 at typical enhanced oil recovery (EOR) conditions is responsible for a poor mobility ratio that causes viscous fingering and poor sweep efficiency, leading to reduced efficiency and yield. One way to overcome this problem is to directly thicken CO_2 . However, the only known polymeric CO_2 thickener (a compound that dissolves in CO_2 and increases it viscosity significantly when present in dilute concentration) is a fluoroacrylate-styrene random copolymer that is too expensive for commercial application. CO_2 has been successfully thickened by dissolution of other high molecular weight polymers like polydimethylsiloxane (PDMS, silicone oil) and polyvinyl acetate (PVAc) but this approach requires several wt% of the polymer along with a large concentration (20%) of co-solvent such as toluene making the method impractical for field use. The alternative to polymeric thickeners are small molecule thickeners that can dramatically increase solvent viscosity at wt% concentrations less than that of polymeric thickeners. Small associative molecules like tributyltin fluoride and hydroxyaluminum di(2-ethyl hexanoate) can thicken light hydrocarbons at concentrations as low as 0.1wt%, but these compounds are CO_2-insoluble. The basic design of new CO_2 thickener candidates designed by our group consists of a small oligomeric CO_2-philic portion to promote dissolution along with CO_2-phobic associative groups to promote viscosity-enhancing intermolecular associations. The biggest hurdle in the molecular design is selecting the appropriate type and number of associating groups needed to enhance viscosity, while maintaining solubility in CO_2. For example, if the associating groups are too weak, the thickening candidate is likely to dissolve in CO_2 but the resultant increase in viscosity will be very modest. If the thickener is modified to include stronger associating groups, it is likely that these functionalities will render the molecule insoluble in CO_2. Many novel CO_2 thickening candidates were synthesized in an attempt to achieve the elusive molecular design that strikes the balance of maintaining solubility in CO_2 at EOR conditions while exhibiting enough self-associations to increase the viscosity of CO_2 significantly at dilute concentrations.