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Effect of nonfluorinated surfactants' hydrophilic tails on CO_2-in-water (C/W) emulsion stabilization

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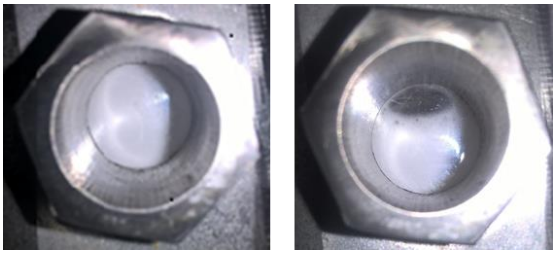
ABSTRACT

Supercritical carbon dioxide is a green solvent. Unfortunately, its low polarizability per volume and low dielectric constant leading usual surfactants cannot stabilize CO_2 in water. Some efficient but toxic and expensive fluorinated surfactants were found to form C/W emulsions. Hydrocarbon surfactants were environmental friendly and in a low cost. However, commercial nonfluorinated surfactants usually required high pressure. Therefore, design for nonfluorinated surfactants was necessary. Our previews work investigated that the enhanced CO_2-philic tails can improve the stability of C/W emulsions by studying poly(vinyl acetate-alt-diethyl maleate)-*b*-poly(dimethylaminoethyl methacrylate) (PVDBM-*b*-PDMAEMA) and poly(vinyl acetate)-*b*-PDMAEMA. The study on the hydrophilic tails of surfactants can also help us to design the green nonfluorinated surfactants to form stable C/W emulsions.

In this work, polyethylene glycol (PEG) was used as hydrophilic tails. The surfactants PVDBM-*b*-PEG_{32} (Mn=2000 g/mol) were synthesized by RAFT/MADIX. Stabilization time for C/W emulsions formed by PVDBM-*b*-PEG_{32} was measured to evaluate the stability of C/W emulsions. It was found that $PVDBM_5$-*b*-PEG_{32} could emulsify 90% CO_2 in H_2O at 25 °C under 20.0 MPa for more than 24 hours, while PVDBM-*b*-PDMAEMA couldn't stabilized such high volume fraction of CO_2 in H_2O under the same condition. In addition, $PVDBM_{3\sim16}$-*b*-PEG_{32} could emulsify 80% CO_2 in H_2O at 25 °C under 12.0 MPa, which was much lower than PVDBM-*b*-PDMAEMA did (20.0 MPa). The results showed that the C/W emulsion stabilized by PVDBM-*b*-PEG was more stable and required less pressure than PVDBM-*b*-PDMAEMA did. The group PEG has a stronger hydrogen bond with water comparing with PDMAEMA leading to a more stable C/W micelle. Meanwhile, the nonionic group PEG's miscibility in CO_2 was better than the ionic group PDMAEMA, which resulted in a lower pressure. In conclusion, strong hydrogen bond with water and high CO_2-philicof hydrophilic tails can improve the stability of C/W emulsions and lower the stabilization pressure.



(Left) stable C/W emulsion; (Right) emulsion breaking.