Program & Abstracts

Petro Phase 2019

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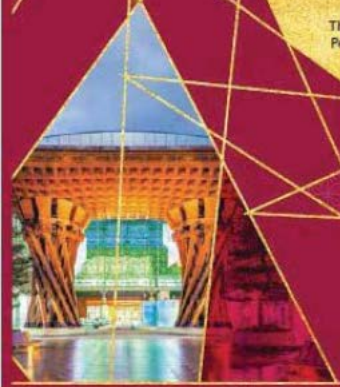

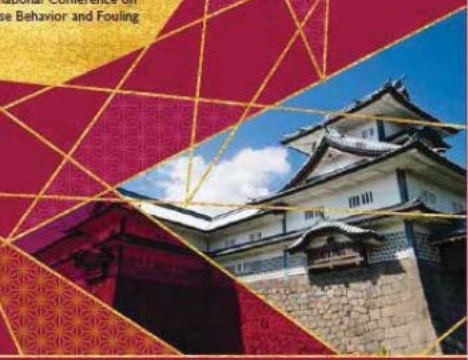

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Emulsification of oil film by the halloysite clay-hydrotrope composites

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Oils and fuels possess the inherent danger to fragile aquatic ecosystems in case of spill. The proper hydrocarbon spill mitigation should include emulsification steps in order to disrupt the oil film, which blocks the oxygen supply to the water, and tends to contaminate the fur and feathers of animals and birds. Known oil dispersants have insufficient efficacy and high ecotoxicity, and thus need to be replaced by novel, safer materials [1]. Environmentally friendly dispersants can be formed using nanocontainers with tunable hydrophobicity loaded with biodegradable amphiphiles – hydrotropes. Hydrotropes act as surfactants but instead of micelles, they form short-lived clusters [2].

Halloysite clay nanotubes may serve as cheap nanocontainers for various functional agents [3]. In addition, halloysite nanotubes, when properly hydrophobized, can stabilize the oil-in-water emulsions [4]. We have modified halloysite with water-soluble adsorbates, and then calcined at 500 – 600 °C to produce the hydrophobized carbon-coated clay nanotubes. The hydrophobized halloysite was then loaded with various hydrotropes and used as dispersant. The emulsifying action of the produced composites was assessed by the optical microscopy of oil-in-water emulsions stabilized with the synthesized dispersants. Crude oil was used at concentration of 20 wt % in simulated seawater and halloysite-based composites were added at 0.8 wt %. The emission kinetics of low molecular amphiphiles were studied by refractometry, the dynamic interfacial tension was measured by spinning drop method.

In the presence of hydrotropes, the interfacial tension between oil and simulated seawater decreases, resulting in stabilization of smaller droplets in oil dispersions. It was observed that the combination of hydrotrope (tert-butanol or butoxyethanol), hydrophobized clay nanotubes, and gas-forming agents ensures the formation and stabilization of oil-in-water emulsion even in the absence of external energy source such as stirring. Halloysite formulations allow for synergistic efficiency by loading existing amphiphile dispersants like Corexit® into the nanotubes.

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(1) Rico-Martínez, R.; Snell, T. W.; Shearer, T. L. Synergistic toxicity of Macondo crude oil and dispersant Corexit 9500A® to the *Brachionus plicatilis* species complex (Rotifera). *Environ. Pollut.* **2013**, *173*, 5–10.
(2) Novikov, A. A.; Semenov, A. P.; Monje-Galvan, V.; Kuryakov, V. N.; Klauda, J. B.; Anisimov, M. A. Dual Action of Hydrotropes at the Water/Oil Interface. *J. Phys. Chem. C* **2017**, *121* (30), 16423–16431.
(3) Panchal, A.; Swientoniewski, L. T.; Omarova, M.; Yu, T.; Zhang, D.; Blake, D. A.; John, V.; Lvov, Y. M. Bacterial Proliferation on Clay Nanotube Pickering Emulsions for Oil Spill Bioremediation. *Colloids Surfaces B Biointerfaces* **2018**, *164*, 27–33.
(4) Owoseni, O.; Bose, A.; Zhang, Y.; McPherson, G. L.; He, J.; Su, Y.; John, V. T. Tuning the Wettability of Halloysite Clay Nanotubes by Surface Carbonization for Optimal Emulsion Stabilization. *Langmuir* **2015**, *31* (51), 13700–13707.

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