The Influence of Low Methanol Concentrations in Surfactant Solutions on Hydrate Anti-Agglomeration

J. Dalton York and Abbas Firoozabadi, Chemical Engineering, Yale University, New Haven, CT 06520

The use of low-dosage hydrate inhibitors(LDHI) is an alternative to thermodynamic inhibitors in preventing gas hydrate formation in pipeline blockage. Anti-agglomerants have been the focus of one recent study(M. L. Zanota, et al., 2005, Energy & Fuels 19, 584) that used a multiple-sample testing apparatus employed with a temperature bath and temperature data acquisition to study crystallization characteristics. In our work, we utilize the same experimental approach and similar type of surfactants.

The purpose of this work is to further examine the effect of various surfactants on the crystallization and agglomeration of tetrahydrofuran(THF) hydrate. A more specific object is to investigate the role of steric effects due to surfactant adsorbed on hydrate crystals. In particular we investigate the effect of small amounts of a thermodynamic inhibitor, methanol, to the mixtures.

A multiple-sample test tube rocking apparatus is employed along with temperature bath and thermocouple data acquisition to determine crystallization characteristics—the characteristics being subcooling from crystallization and melting temperatures as well as the time required for crystallization. Visual inspection is also made of the agglomeration state of the fluid mixtures at their lowest temperatures; observations show a clear distinction between what is deemed as a hydrate plug and a mixture where proper anti-agglomeration is occurring.

Mixtures of water/methanol/THF/oil/surfactant with various concentrations of methanol are used. We also perform tests to study crystallization of mixtures of water, THF, and methanol. The various surfactants used in our work are mostly of quaternary ammonium type; the group does include a biosurfactant, and nonionic surfactants—effective as anti-agglomerants in pure water/ice and emulsifiers. Only 2,2,4 trimethylpentane is used as the oil phase.

Results show the effect of low methanol concentration on the THF hydrate crystallization in the presence of surfactants. Other studies (M. Pakulski and D. Hurd, 2005, Proceedings of the Fifth International Conference on Gas Hydrates, Trondheim, Norway, June 13-16; E. D. Sloan, et al., 1998, Ind. Eng. Chem. Res. 37, 3124) have reported kinetic data for hydrate mixtures in the presence of surfactant or polymer showing evidence that the addition of small amounts of methanol has a significant effect on subcooling and gas consumption rate.

A theoretical framework based on interfacial thermodynamics, Flory-Huggins theory, and principles from colloid science has been developed to provide

theoretical analysis of data and interpretation of results. A mathematical model for steric repulsion between two, surfactant-coated surfaces in binary and ternary mixtures with methanol and/or oil as solvent is described. Steric repulsion calculations were made with only binary Flory-Huggins interaction parameter values from experiment. This repulsive term coupled with an attractive potential due to van der Waals forces is used in the analysis.

Abstract ID#: 66041 Password: 243825 Title: The Influence of Low Methanol Concentrations in Surfactant Solutions on Hydrate Anti-Agglomeration Session Selection: 01C01 Colloidal Dispersions II - Stability & Dispersion Preferred Presentation Format: Oral Lead Presenter's Email: john.york@yale.edu

First Author

Presenting Author

J. Dalton York Graduate Research Assistant Chemical Engineering Yale University New Haven, CT 06520 **Phone Number:** 860-463-3428 **Email:** john.york@yale.edu

Second Author

Abbas Firoozabadi Adjunct Professor Chemical Engineering Yale University New Haven, CT 06520 **Phone Number:** 203-432-4379 **Email:** abbas.firoozabadi@yale.edu