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Studies of the Dynamics in and the effect of surfactants on gas hydrates formation and agglomeration.

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Objective: To determine the effect of series and parallel hydrate particle agglomeration on the electrical impedance of gas hydrates using the liquid droplet on a heated wire (hot wire) technique.

Methodology and Result: The primary conditions necessary for the "hot wire" method of forming hydrates are steady temperatures around 5°C, and an environment capable of containing reactive additives such as cyclopentane. The approach to satisfying these conditions was to create an environment made of aluminum (not reactive with cyclopentane), through which the 'hot wire' would run. To test the hydrate formation on the wire we started with water droplets in series on the 'hot' wire in the presence of cyclopentane. The wire was held at 3A, 3°C and hydrate formation took 2 days. As shown in Figure 1, the hydrates formed on the wire were asymmetrical in shape and off-centered of the wire. We repeated the process several times and were able to have three centered and symmetric hydrates on the wire. We then determined the impedance spectrum for the hydrates on wire and the bare wire, both results are shown in Figure 2.

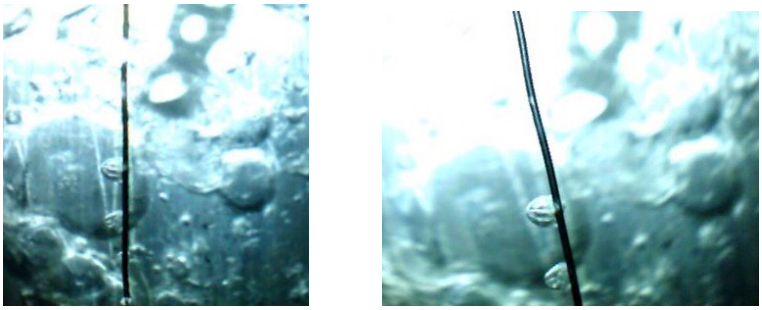

Figure 1. Cyclopentane hydrates formed on 'hot wire'.

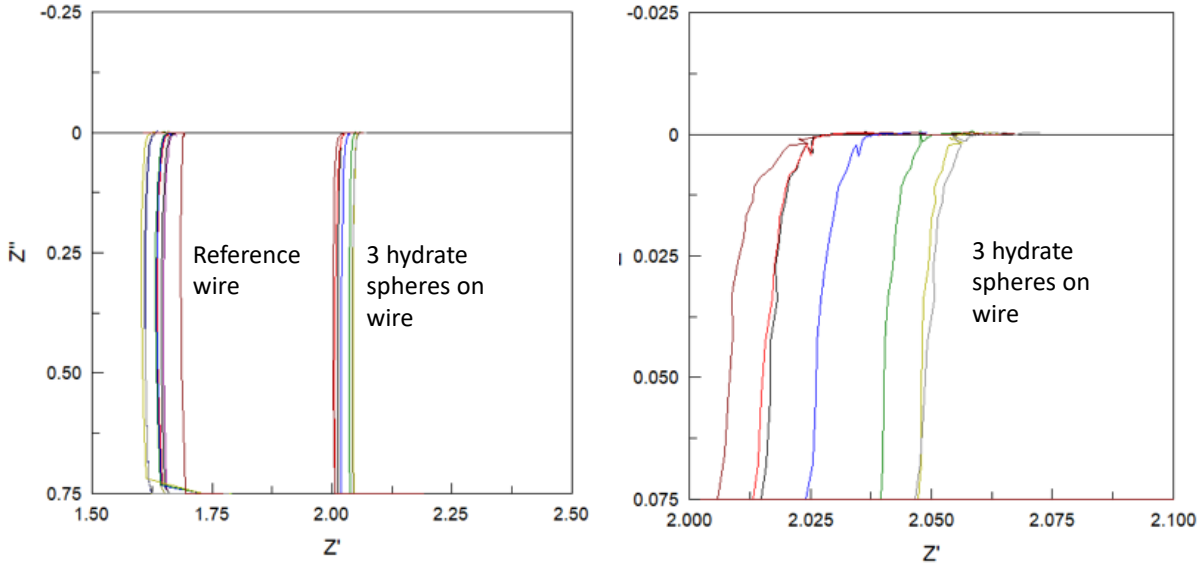

Figure 2. Left – Impedance of 3 hydrates in series on a Nichrome wire (right) versus reference data with no hydrates (left). **Right** – Expanded view of Impedance of three hydrates on a Nichrome wire.

As shown in Figure 2, the hydrates caused an increase in the measured impedance compared to that of the hydrate-free wire. However, with repeated measurements there was a slight decrease in the impedance of the hydrate. At this point the origin of this shift is unknown, but it might be due to the slight increase in temperature in the cyclopentane chamber. Although we are still in the infancy stage with many variables of exploration still outstanding, what we

have determined so far is the following: (1) hydrate formation on the wire takes about 24 hours, and (2) their presence on the wire is detectable by impedance measurements – which is proof of one of the objectives of the proposed work.

NMR Characterization: Hydrates were also allowed to form on the base of the aluminum chamber by dropping water droplets into the chamber containing cyclopentane. We then collected and characterized these hydrates using ^{1}H NMR spectra and spin-lattice relaxation time (T_1). For comparison and proper identification, we also characterized cyclopentane and finely crushed ice. Below in Figure 3 are spectra for water, cyclopentane and the hydrate taken at 5^{o}C. Additionally, the spectra for ice at 0^{o}C was also determined. The water spectrum is centered at 0 ppm while the cyclopentane is shielded at -3.08 ppm. The hydrate spectrum contains two asymmetric regions that can clearly be assigned to the cyclopentane and water hydrate. The ice spectrum is also asymmetric with a very broad component and an overlapping narrower component. It should be noted that the ice spectrum was collected with four the number of scans used for the hydrate spectrum. It should also be noted that the hydrate collected contained liquid cyclopentane which accounts for its presence in the spectrum. That said, although the hydrate spectrum bears some similarity to the ice spectrum, the chemical shift and lack of broad component suggest a mobile albeit rigid structure comprised of water molecules, as is expected for a water hydrate.

The verification and mobility were further emphasized by the T_1 data, which was 2.1 ± 0.027 sec and 3.77 ± 0.13 sec for the hydrate and cyclopentane peaks respectively. The T_1 values for pure cyclopentane, water and ice were 3.74 sec, 3.7 sec and 0.3 sec respectively. This provides further indication that the hydrate was actually formed.

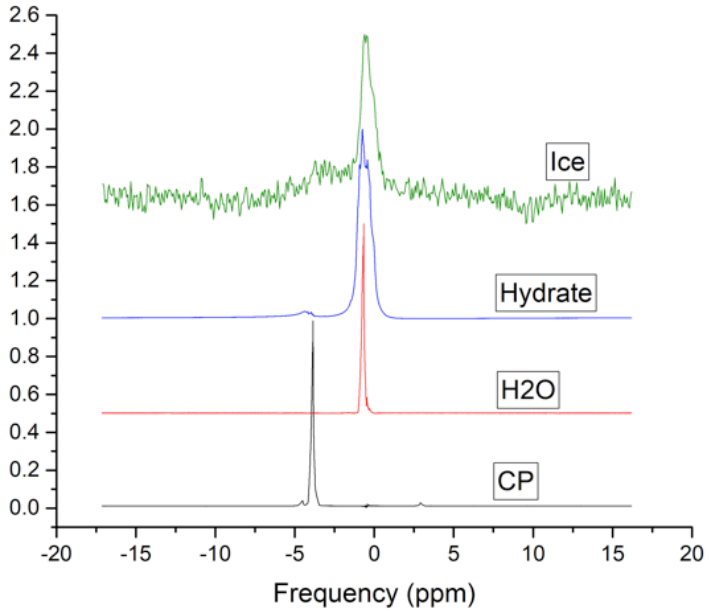

Figure 3. ^{1}H NMR spectra for water, cyclopentane and the hydrate, all at 5^{o}C. Ice at 0^{o}C is also shown for comparison.

Next steps:

1. NMR characterization will continue on hydrates formed. We will use additives such as tetrahydrofuran (THF), alkyl polysaccharide glycoside (APG), potassium oxalate monohydrate (POM), methanol, ethanol, neohexane (NH), cyclopentane (CP), and methylcyclohexane (MCH) in forming hydrates, and characterize them using multi-nuclear NMR spectra and T_1 measurements. We will also incorporate gases such as CO_2 to see the effect on hydrate formation and molecular transports.
2. The wire diameter, coating, current, hydrate formation time, and additive will be varied to determine the effect on hydrate formation. The impedance will then be determined for the various arrangements of hydrates.
3. Resolve the issues affecting the impedance measurements and use droplet size, the number of droplets, the arrangement of the droplets (series or parallel), the hydrate former, the presence and type of surfactants and/or gas in water as variables.
4. Publish resulting data.