Cooperative discovery with multiphase microreaction engineering and *in situ* Raman spectroscopy

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Highlights

- Microfluidic spectroscopic studies of liquid-liquid, gas-liquid, and solid-liquid interfaces.
- Discovery of rarefaction, mixture, and shockwave interfacial zones and their thicknesses
- The contribution of mass transport in methane (sI) hydrate crystal growth kinetics.
- Direct measurement of asphaltenes nanosheet size and occupancy distributions in microfluidic porous media.

1. Introduction

Engineering novel tools for the discovery of science and translation of the new knowledge from the laboratory to application are societal challenges. Our laboratory helps address these challenges through the design of novel experimental methodologies for direct measurements in flow. Our ability to acquire information in flow has the potential to reduce the amount of chemical waste generated, minimize the building space and energy requirements, expedite information, and yield more accurate predictive mathematical models during discovery, development, and manufacture. This so called "process intensification" has merit to revolutionize our understanding of chemicals and materials that have global impacts. Microsystems with *in situ* characterization techniques can be considered as the appropriate experimental tools, and the systems are often heterogeneous.

2. Methods

In the present work, microfluidic devices were designed to isolate liquid-liquid, gas-liquid, and solid-liquid interfaces and integrated with confocal Raman spectrometry. The Horiba LabRam HR evolution, Jobin-Yvon on a TMC optical table was equipped with a 532 nm laser, a magnification of 10x (MPlanN Olympus, 0.25 NA, 10.6 mm WD), CCD Synapse EM detector, and Horiba's DualScan and Swift technologies. All spectra were recorded with Labspec V6, and the results were processed using MATLAB R2016a with GSTools and iSignal. All chemicals, including gases, were research grade and purchased from commercial vendors. High purity water was generated using a Milli-Q system (Millipore). In the case of asphaltenes, Wyoming field deposits were obtained from Nalco Champion, An Ecolab Company. Syringe pumps (Harvard Apparatus PHD Ultra Syringe Pumps, or Teledyne ISCO 65DM) were used to inject liquids into the devices using 1/16 O.D. tubing (stainless steel or PEEK). Pressure, temperature, and flow-rates were recorded using an acquisition board (National Instruments, cDAQ-9171) and a LabView code developed in-house. The pressures were controlled using an IDEX back pressure regulator, while the temperature was controlled by PID controllers coupled to thermoelectric modules.

3. Results and discussion

Microfluidics with *in situ* Raman spectroscopy for the investigation of immiscible non-polar/aqueous interactions were designed. A dynamic aqueous phase in contact with a static hydrophobic phase (semi-flow) was engineered on-chip, and it was validated using high-resolution *in situ* Raman spectroscopy. The semi-flow microfluidic device isolated non-polar solvents in a series of micro-reservoirs that communicated with

aqueous laminar flows *via* molecular diffusion (or *vice versa* in the case of methane-water studies). Consequently, inspections of concentration and density profiles from the bulk-to-bulk of toluene-, diethyl ether-, xylenes-, and methane-water were possible. Remarkably, the interfaces were comprised of rarefaction, mixture, and shockwave zones. Evidence of molecular rearrangements at the interface support that we still have much to learn on interfacial reaction chemistry. [1, 2]

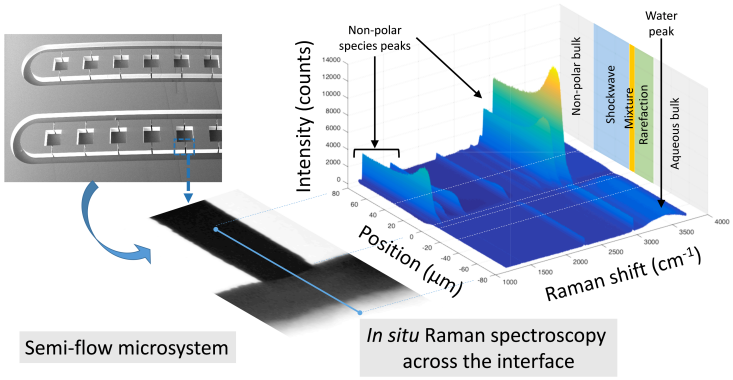

Figure 1. Design of microfluidics with *in situ* Raman spectroscopy can provide new insights in chemical reaction engineering [Reproduced from [1], with permission of The Royal Society of Chemistry].

Materials for the energy sciences were also investigated. Microfluidics with *in situ* characterizations revealed that methane (sI) hydrate nucleation can be achieved in seconds *via* temperature cycling with a thermoelectrically-cooled microreactor. A crystal growth model was derived, and mass transport limitations were found to be significant by estimations of the Lewis (*Le*), Hatta (M_H), and beta (β) numbers. Direct measurements of asphaltenes accumulations in microreactors packed with quartz particles were also made. Deconvolution of the Raman spectra discovered the nanosheet size distribution and the occupancy of these aromatic compounds that form ordered structures within porous media. The injection of zeolite nanoparticles of different Al_2O_3/SiO_2 ratios revealed that the acidity within the packed-bed influences the nanosheet size distribution. Our discoveries lay the groundwork for the next generation of high-throughput understanding of materials in the energy and the environmental sciences. [3, 4]

4. Conclusions

This talk will focus on our recent discoveries of i) liquid-liquid and gas-liquid microfluidics with *in situ* Raman spectroscopy and ii) integrated microsystems design for crystallizations in the energy and environmental sciences. Reaction interfaces confined in micro-scale flows sometimes behave differently than unconfined ones. In response, our recent work on the design of microfluidics with *in situ* Raman spectroscopy to understand confined non-polar solvent/water and methane/water interfaces will be presented. Microsystems with online spectroscopic methods also have tremendous potential for understanding materials in the energy and environmental sciences. Flash crystallizations of methane hydrates with high-pressure, sub-cooled microsystems can reveal the contribution of mass transport on the crystal growth kinetics. Crystallizations of asphaltenes, high-molecular weight aromatics, are a challenge to characterize in porous media. Packed-bed microfluidics with online analytics can yield the direct measurement of nanosheet size and occupancy distributions. The seminar will conclude with a brief discussion of emerging trends.

References

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Keywords
Microsystems; multiphase; *in situ*; Raman spectroscopy.