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Characterization of Crude Oil Emulsions by Cryo Electron Microscopies

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Water in oil forms emulsions during crude oil production and degrades the product quality as well as poses a technical challenge to oil industry. In order to achieve a specified product quality, the oil/water emulsion formation must be resolved. One of the most important features of a crude oil emulsion is its droplet size distribution (DSD). The DSDs determine the stability of emulsions and hence must be considered when choosing optimized treatment protocols [1]. There are various methods including near-infrared light, optical microscopy, confocal laser scanning microscopy and nuclear magnetic resonance that are being used currently to characterize the DSDs of emulsions [2]. However, limited spatial resolution and/or lack of direct visualization of droplets diminish reliability and quality of measurements made by these techniques. Electron microscopy provides a method for the direct visualization of structures with highest spatial resolutions and therefore can be used in determining the DSDs of emulsion droplets more accurately.

We used cryo scanning electron microscopy (cryoSEM) and cryo transmission electron microscopy (cryoTEM) to examine crude oil emulsions. A Nova NanoSEM (FEI Company) equipped with a cryo preparation chamber (Quorum Technology) was used for imaging the emulsions droplets in natural hydrated state. Prior to imaging, the emulsions were cryo-fixed, freeze fractured and then sublimed to reveal the internal structure of droplets. A Quanta 3D dual beam SEM (FEI Company) equipped a cryo-preparation chamber was used to prepare cross sections of cryo-fixed emulsions free of artifacts for examining the droplets at low temperatures. The emulsions were also investigated with a cryoTEM instrument of model Titan G^2 80-300CT S/TEM (FEI Company) to find the presence of deep submicron size emulsion droplets and to determine the nature of water and oil mixing in those droplets. This was achieved by freezing the emulsion-loaded Quantifoil™ copper grids comparatively slowly in order to have the water content solidified to crystalline ice as supposed to vitrified ice. The crystalline ice in the emulsion droplets will exhibit the diffraction or modulating image contrast.

CryoSEM imaging of the freeze fractured plane of emulsion showed the presence of droplets that ranged from 200 to 5 µm in diameters (Fig. 1A). Freeze fracturing of emulsions followed by sublimation revealed a complex meshed-network of organic materials that formed the internal structure of droplets. CryoSEM analysis also indicated that the water was confined within this network. Due to rough fractured planes of emulsions after freeze fracturing, it was not possible to observe the droplets smaller than 5.0 µm in diameter. Emulsion cross sections prepared by cryo-FIB milling showed the presence of droplets that ranged from 10 to 1 µm in diameters (Fig. 1B). FIB-milled emulsion droplets after sublimation showed a meshed network of organic materials that was similar to that of larger ones (200-5 µm). Application of cryoTEM in bright-field TEM mode on emulsion revealed the presence of droplets that were smaller than 1.0 µm in diameter (Fig. 2). The contrast modulations in the droplets were result of electron diffraction by crystalline phase of water in the droplets.

In summary, we demonstrated that the cryo electron microscopies are suitable to determine the DSDs of emulsions droplets. We were able to characterize droplets ranging from many tens of microns to submicron in diameters. The cryoSEM imaging after freeze-fracturing and cryoFIB milling showed the presence of water and organic phases in the droplets. Finally, cryoTEM confirmed the water confinement in submicron size droplets.

References:

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[2] G. Van Dalen. Journal of Microscopy, 208(2002), p116.

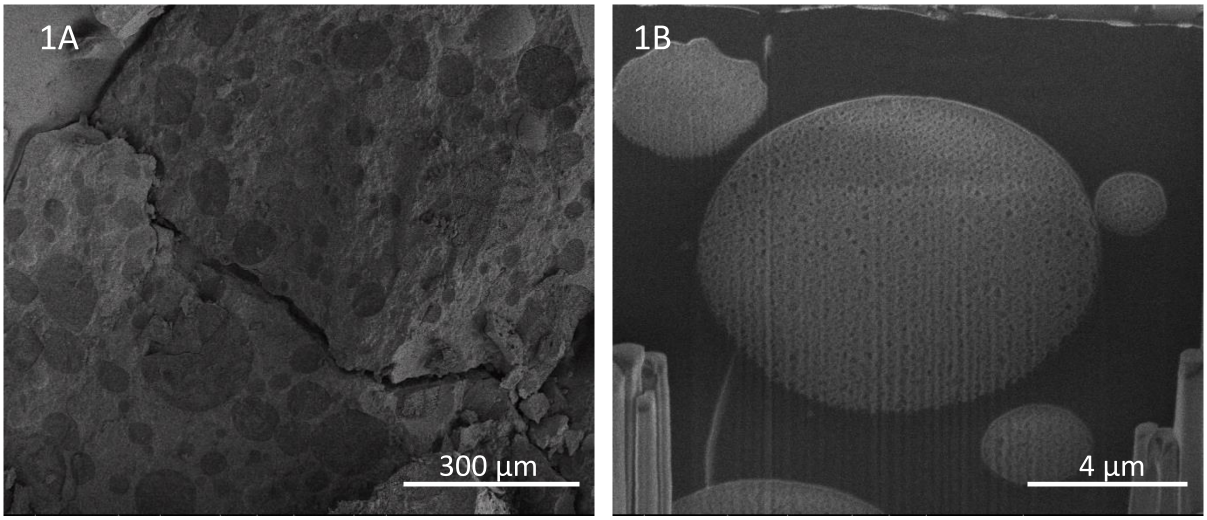

Fig. 1: CryoSEM images of emulsion droplets after freeze fracture (A) and FIB-milling (B) showing droplets ranging from 200 to 1 µm in diameters.

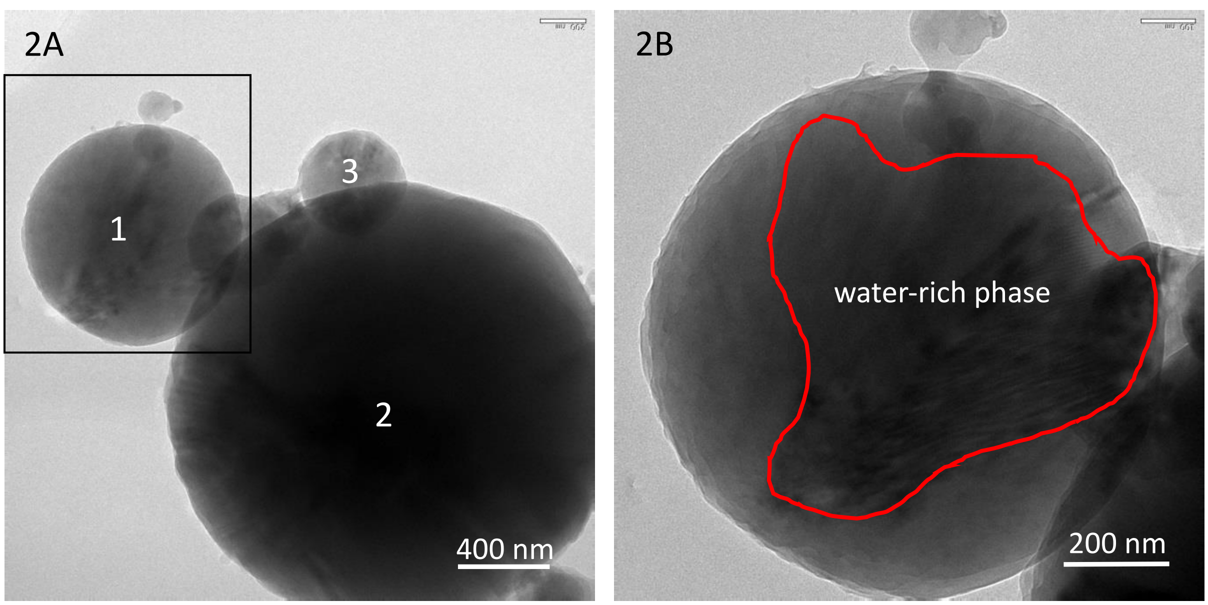

Fig. 2: CryoTEM images of emulsion droplets in bright-field-TEM mode using 300 keV energy electron beam. (**A**) Submicron size droplets (labeled as “1” and “3”) are suitable for TEM analysis. (**B**): A higher magnification of boxed area in A showing water-rich phase within the droplet (enclosed by “red” lines).