13 Πανελλήνιο Επιστημονικό Συνέδριο Χημικής Μηχανικής

Polymer-coated Nanoparticles used as agents for Enhanced Oil Recovery

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FORTH INSTITUTE OF CHEMICAL ENGINEERING SCIENCES

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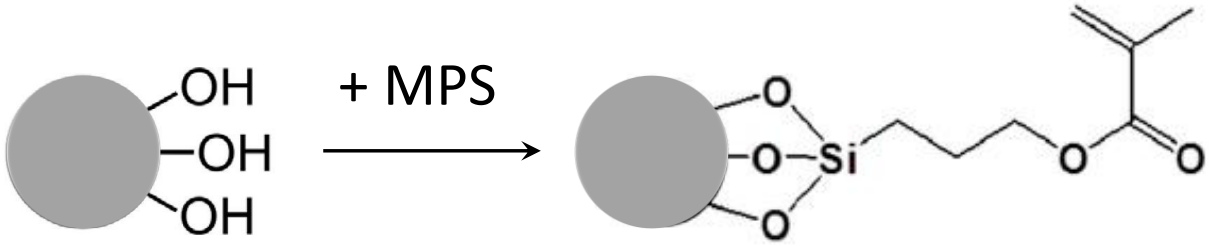
- PNPs Characterization
- Surface/Interfacial Tension and Rheology Characterization
- Displacement Tests

Polymer-coated nanoparticles (PNPs)

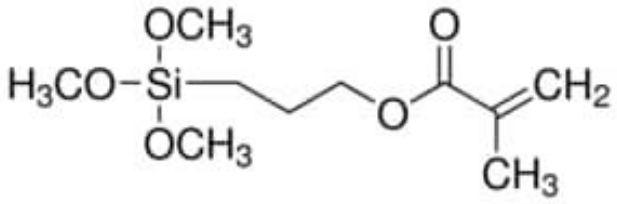
1) Functionalization of SiO_2 NPs with 3-(trimethoxysilyl)-propyl methacrylate (SiO_2-MPS)



SiO_2 SiO_2-MPS

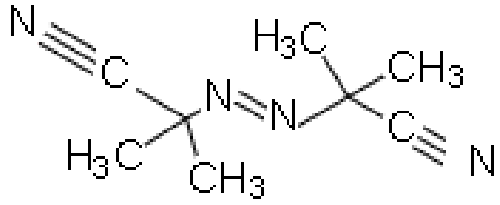
- ✓ SiO_2 NPs in toluene-sonication
- ✓ add MPS under vigorous stirring
- ✓ stirring and reflux at 100 °C for 24 h
- ✓ separated by centrifugation at 9000 rpm
- ✓ three "wash by EtOH/centrifuge" cycles
- ✓ dry in vacuum oven at 60 °C overnight

MPS :



3-(methacryloxy)propyltrimethoxysilane

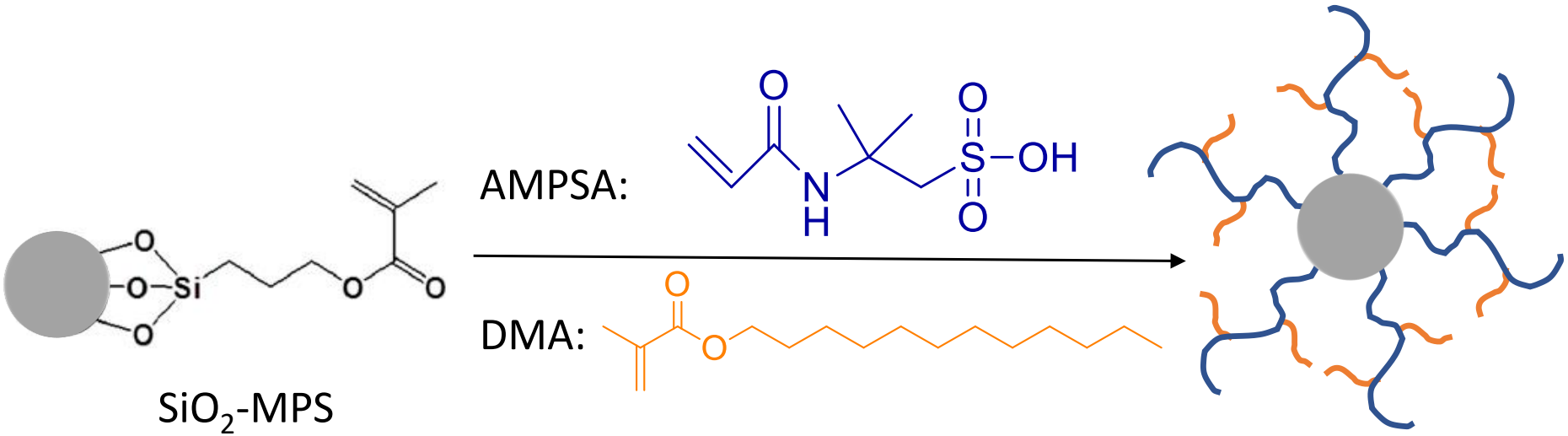
AIBN:



Azobisisobutylronitrile

Polymer-coated nanoparticles (PNPs)

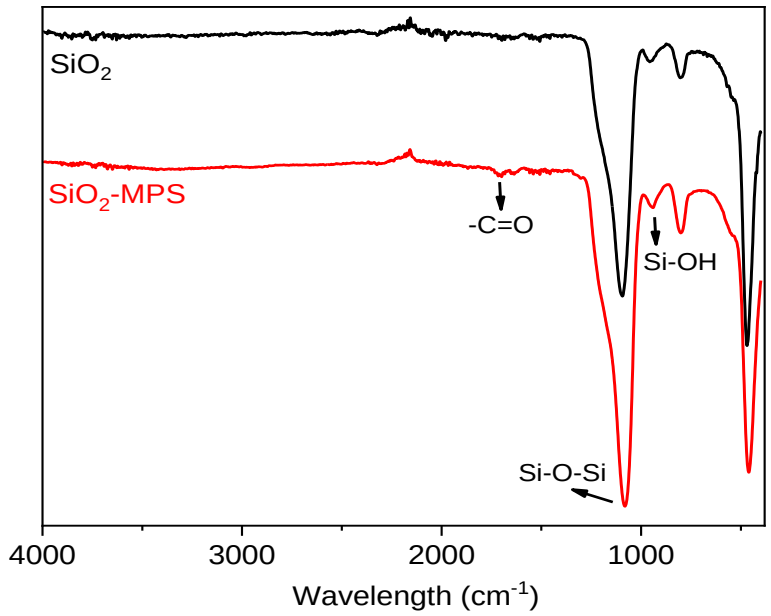
2) Polymerization of AMPSA and DMA monomers onto the functionalized SiO_2-MPS NPs (SiO_2-P(AMPSA-co-DMA))



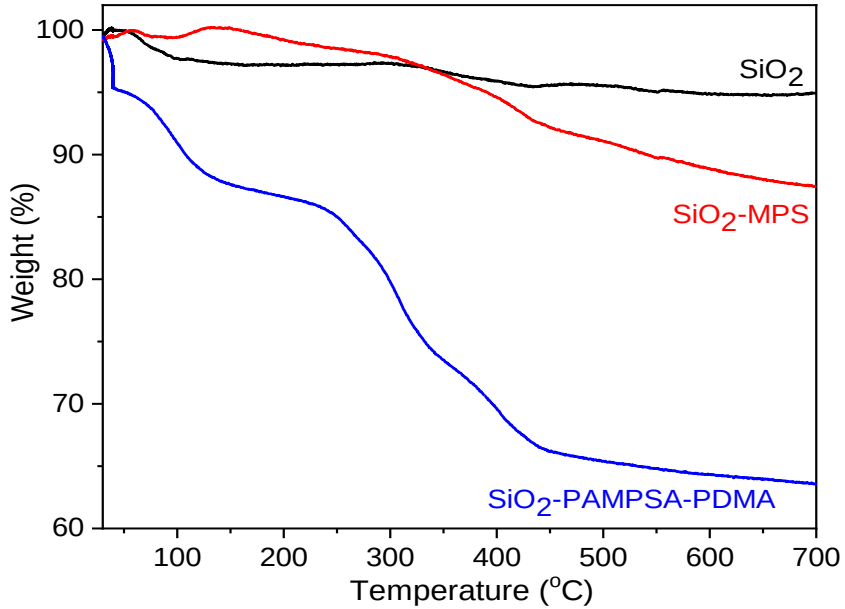
- ✓ dispersed SiO_2-MPS NPs in DMF - sonication
- ✓ add AMPS and DMA monomers and initiator AIBN
- ✓ stirring under N_2, at 80 °C for 24 h
- ✓ separated by centrifugation at 11000 rpm
- ✓ three "wash by H_2O/centrifuge" cycles, dry in vacuum oven at 50 °C overnight

PNPs Characterization

ATR-FTIR



TGA



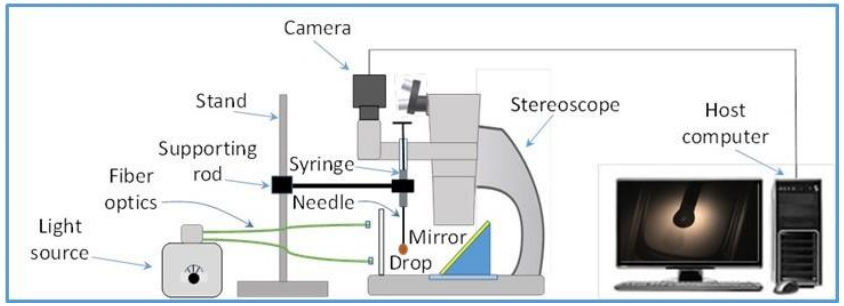
<u>In both SiO_2 and SiO_2-MPS :</u>
1095 and 465 cm^{-1} : asymmetric stretching vibration of Si-O-Si groups of silica
955 cm^{-1} : vibration of Si-OH groups of silica
<u>In SiO_2 -MPS NPs :</u>
1640 cm^{-1} : new stretching vibration peaks of C=C groups from MPS
1715 cm^{-1} : stretching vibration peaks of C=O groups from MPS

✓ Successful surface modification of the SiO_2 NPs by MPS and at a next step by P(AMPSA-co-DMA)

Surface Tension Characterization

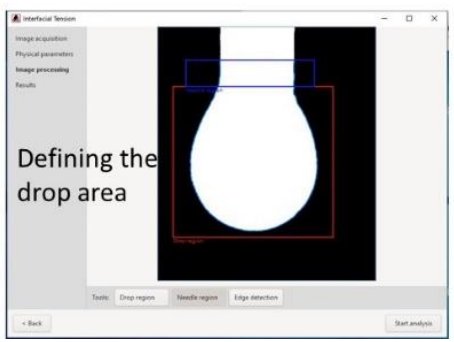
Pendant Drop Method:

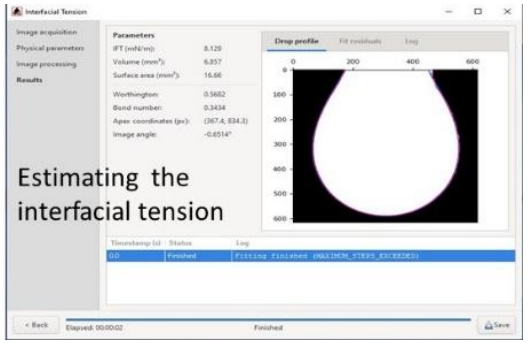
Dynamic Surface and Interfacial Tension of nano-colloid suspensions



Experimental setup of pendant drop method

analyzing the recorded interfacial configurations with the open access OpenDrop software of inverse modeling of Young-Laplace equation



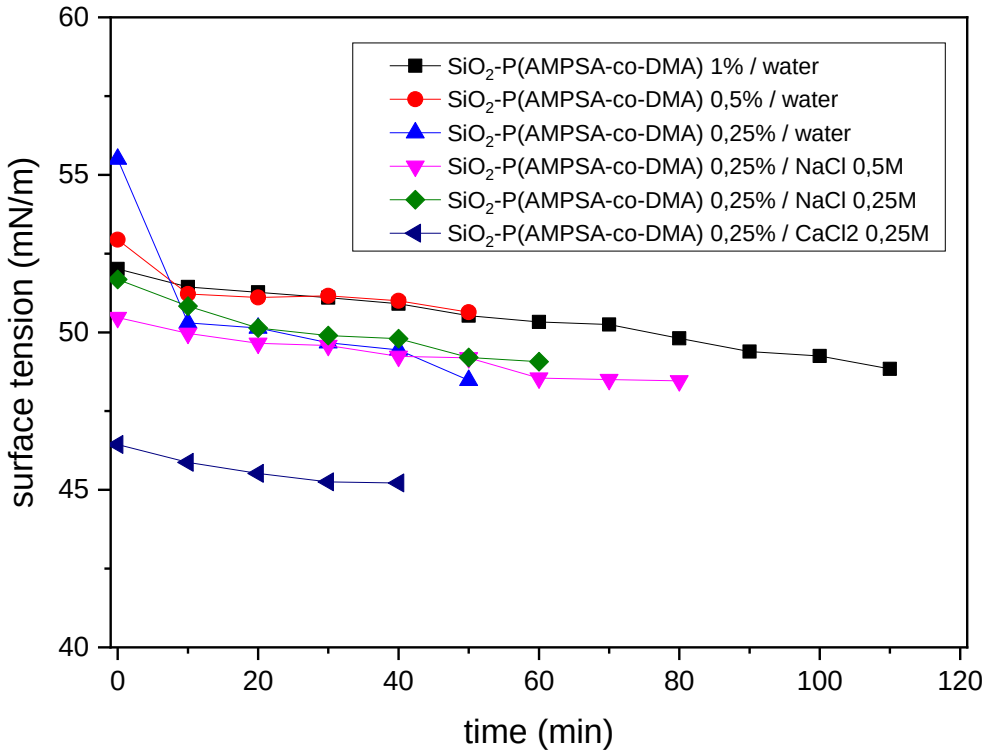


Estimation of surface/interfacial tension by OpenDrop software

Berry, J.D., et al. (2015). *J. Colloid Interface Sci.* 454: 226-237.

Surface Tension Characterization

Dynamic surface tension (ST) as function of time for various concentrations of SiO_2-P(AMPSA-co-DMA) NPs in water and salt solutions (NaCl, $CaCl_2$).

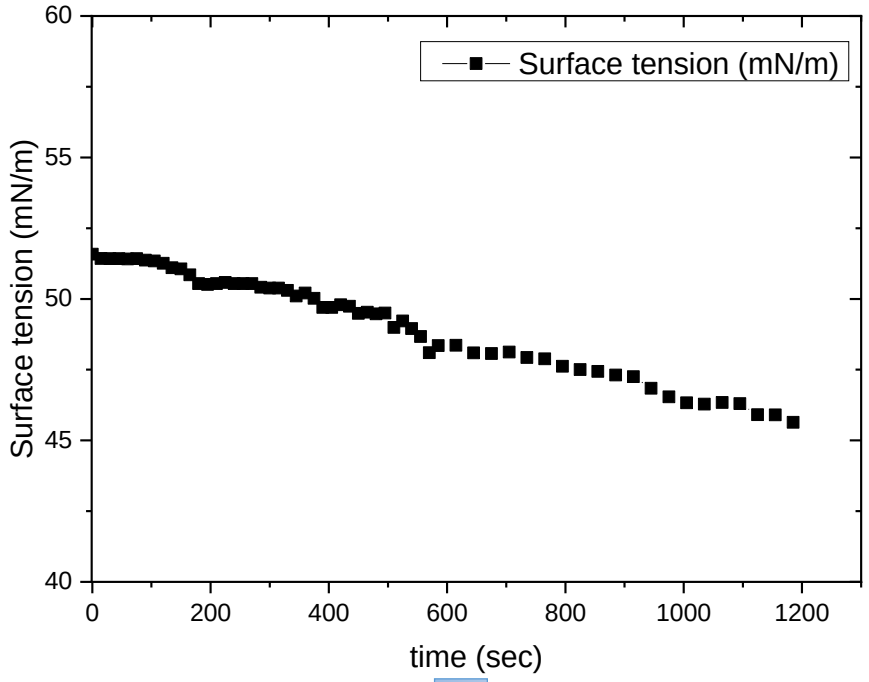


- Maximized reduction rate of ST of SiO_2-P(AMPSA-co-DMA) NPs at PNP concentration equal to 0.25%
- with the addition of NaCl, the ST changes weakly
- with the addition of $CaCl_2$, the ST drops significantly, due to the stronger electrostatic interactions of the divalent $CaCl_2$ with the P(AMPSA-co-DMA) polyelectrolyte and increased ionic strength

Surface Tension and Rheology Characterization

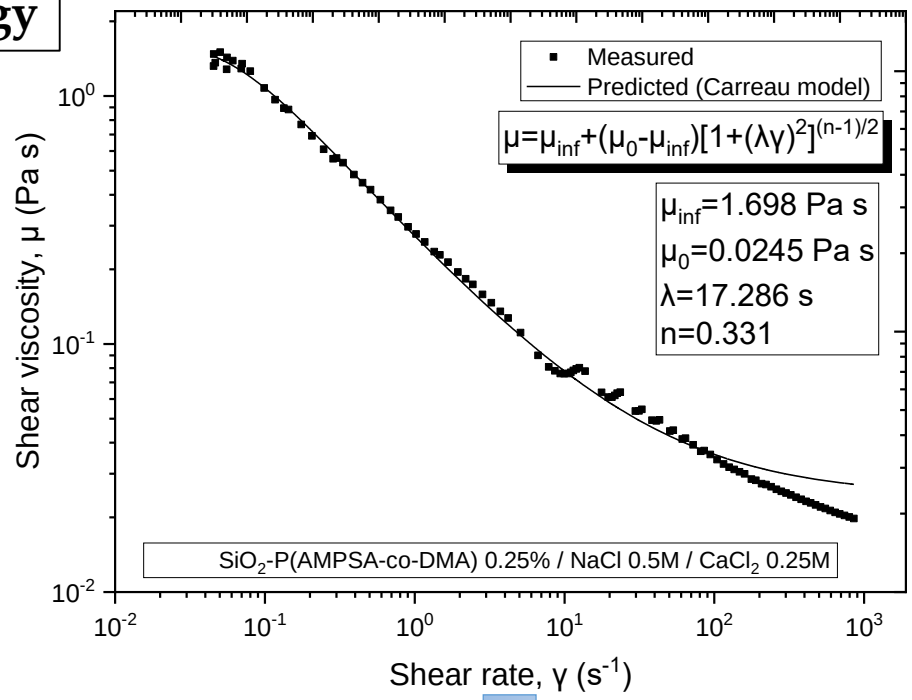
PNP dispersion: SiO_2-P(AMPSA-co-DMA 0.25% / NaCl 0.5M / $CaCl_2$ 0.25M

ST



respectable reduction rate of ST with time

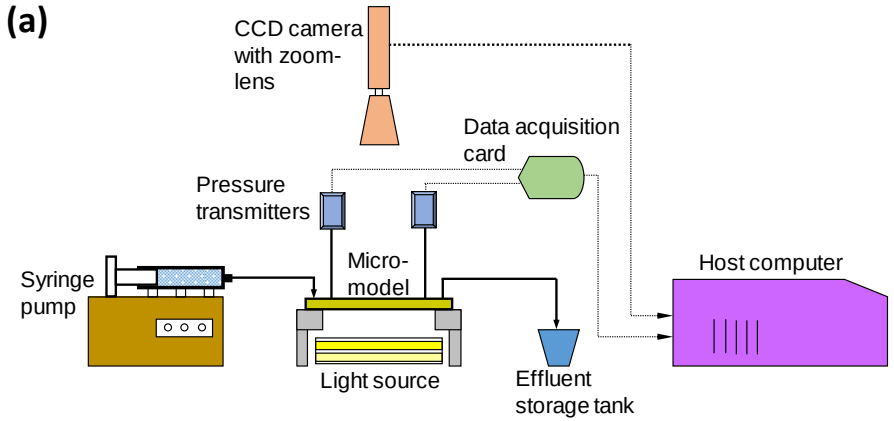
Rheology



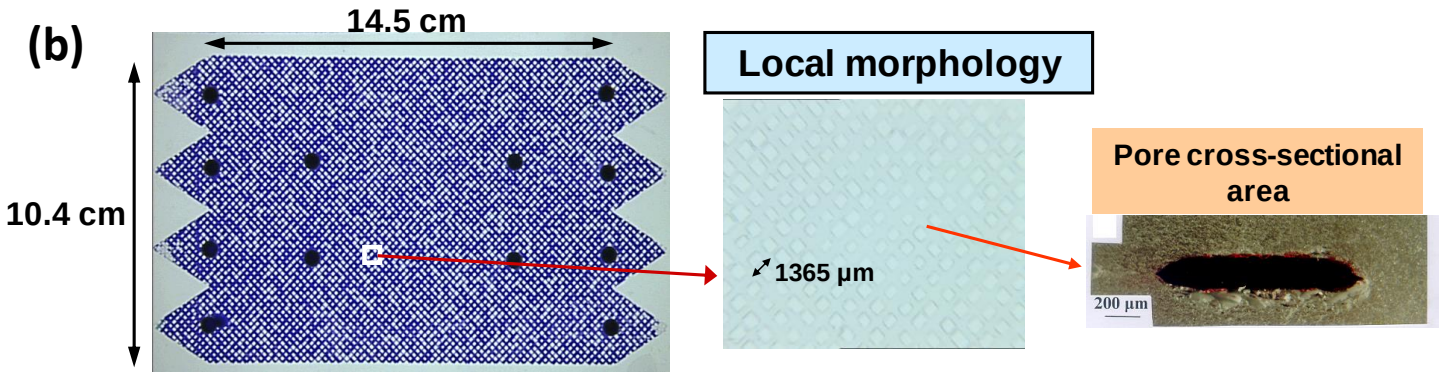
The shear thinning rheology of the Pickering emulsion was fitted satisfactorily with the Carreau model

Displacement Test

Visualization EOR tests in a glass-etched pore network



(a) Schematic diagram of experimental setup.



(b) Morphology of glass-etched pore network model.

Displacement Test

Displacement Tests conducted on the glass micromodel

Transient responses of **paraffin oil saturation** and **pressure drop** across the central area of the pore network for successive displacement tests,

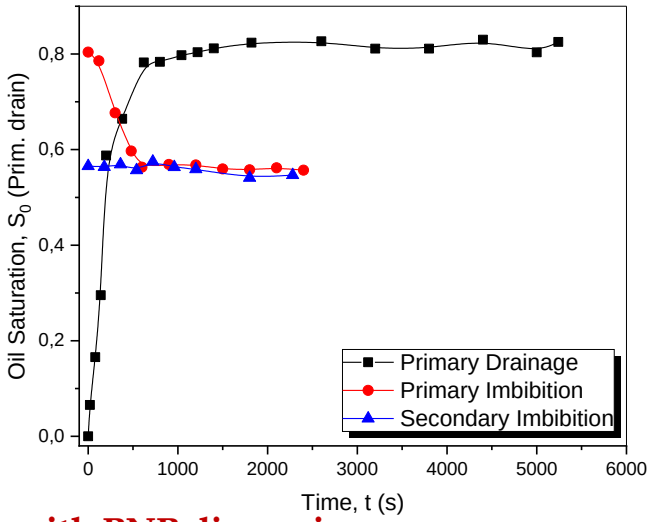
- **brine :** aqueous solution of NaCl 0.5M and $CaCl_2$ 0.25M
- **displacing fluid in secondary imbibition step :**

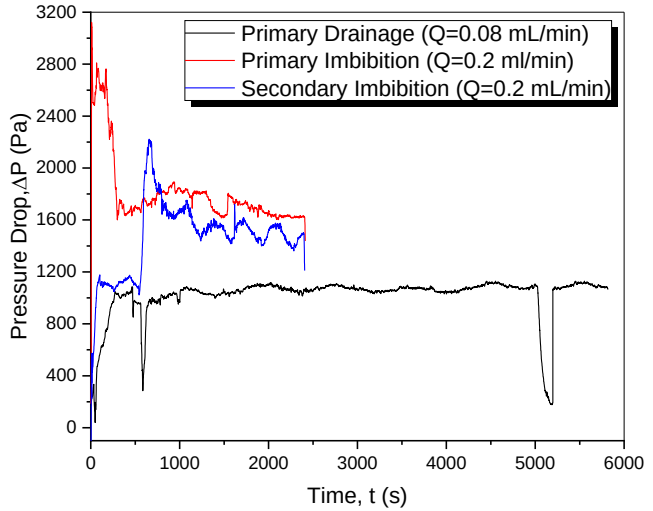
➢ the PNP dispersion [SiO_2-P(AMPSA-co-DMA) 0.25% / NaCl 0.5M / $CaCl_2$ 0.25M]

or

➢ Pickering emulsion along with PNP dispersion, injected at equal flow rates

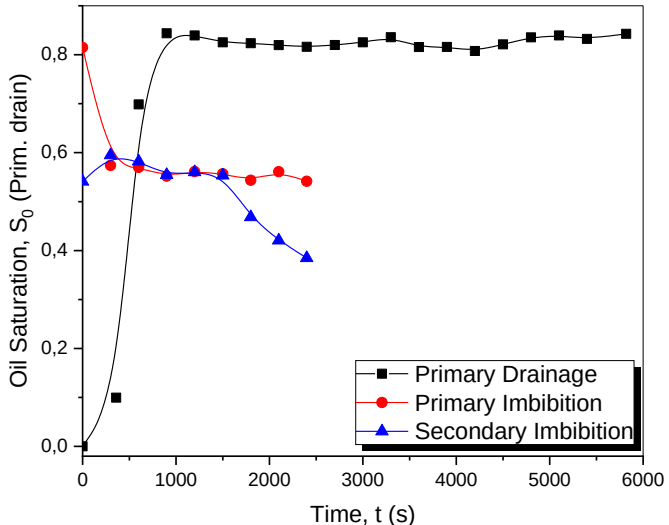
[SiO_2-P(AMPSA-co-DMA) 0.25% / NaCl 0.5M / $CaCl_2$ 0.25M] dispersion

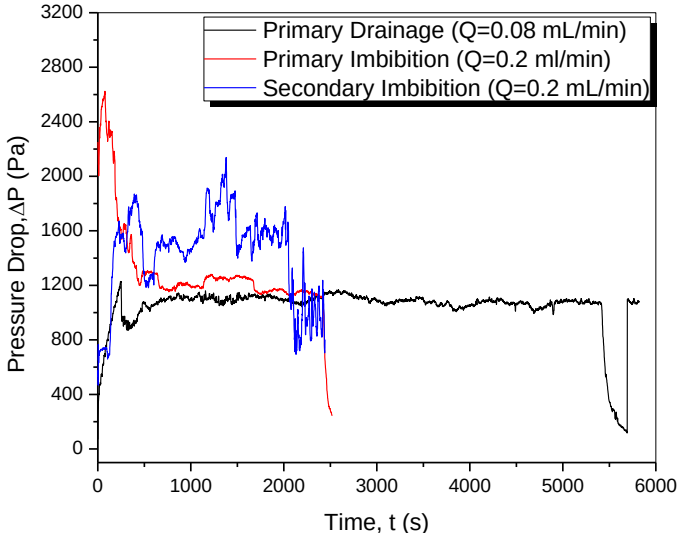




relatively low EOR efficiency was achieved with the PNP dispersion

Pickering emulsion along with PNP dispersion



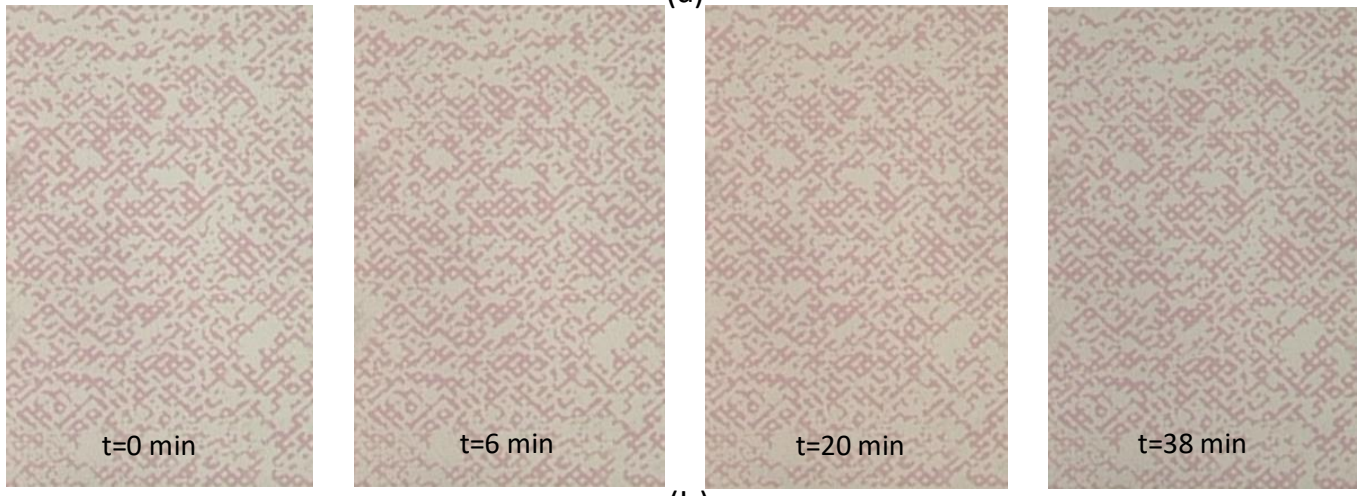


significant EOR efficiency achieved by injecting simultaneously emulsion and PNP dispersion at equal flow rates

Successive snap-shots of the displacement of residual paraffin oil (secondary imbibition) by:

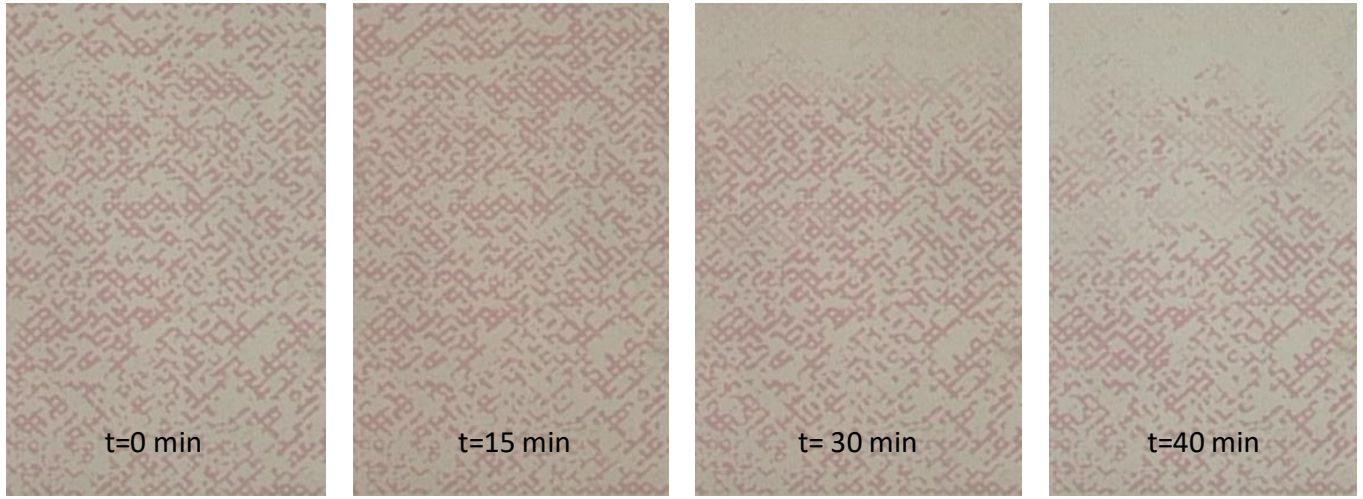
(a)

[SiO_2-P(AMPSA-co-DMA) 0.25% / NaCl 0.5M / $CaCl_2$ 0.25M] dispersion



(b)

Pickering emulsion along with PNP dispersion



Better displacement: the presence of the viscous emulsion facilitates the displacement of the viscous paraffin oil

Conclusions

- Successful surface functionalization of SiO_2 NPs by MPS and P(AMPSA-co-DMA) copolymer
- Surface tension depends on the concentration of SiO_2-P(AMPSA-co-DMA) PNPs
  - with the addition of NaCl, the ST changes weakly
  - with the addition of $CaCl_2$, the ST drops significantly
- Relatively low EOR efficiency was achieved with the SiO_2-P(AMPSA-co-DMA)0.25% / NaCl 0.5M / $CaCl_2$ 0.25M PNP dispersion
- Significant EOR efficiency achieved by injecting simultaneously Pickering emulsion and PNP dispersion
- Better displacement of paraffin oil was exhibited by the Pickering emulsion along with the PNP dispersion: the presence of the viscous emulsion facilitates the displacement of the viscous paraffin oil

Acknowledgments

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EORPNP

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