3rd International Conference on Environmental Design, ICED2022

Polymer-coated Nanoparticles used as agents for Enhanced Oil Recovery

Ch. Ntente [1,2], A. Strekla [1,3], Z. Iatridi [1,2], M. Theodoropoulou [1], G. Bokias [1,2] and Ch. Tsakiroglou[1,*]

[1] Foundation for Research and Technology Hellas, Institute of Chemical Engineering Sciences (FORTH/ICE-HT), 26504 Patras, Greece

[2] University of Patras, Department of Chemistry, 26504 Patras, Greece

[3] University of Patras, Department of Physics, 26504 Patras, Greece

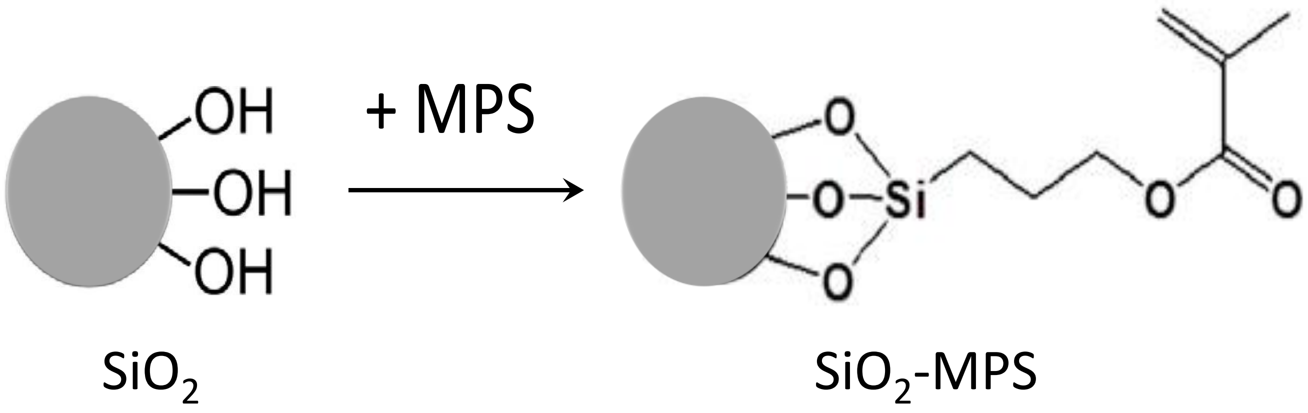
FORTH INSTITUTE OF CHEMICAL ENGINEERING SCIENCES

UNIVERSITY OF PATRAS
ΠΑΝΕΠΙΣΤΗΜΙΟ ΠΑΤΡΩΝ

Contents

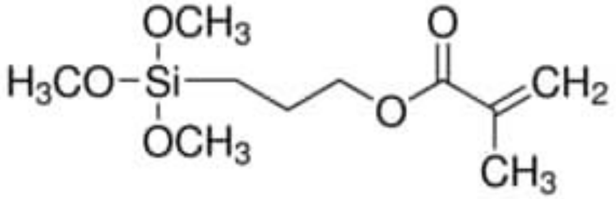
Polymer-coated nanoparticles (PNPs)

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



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

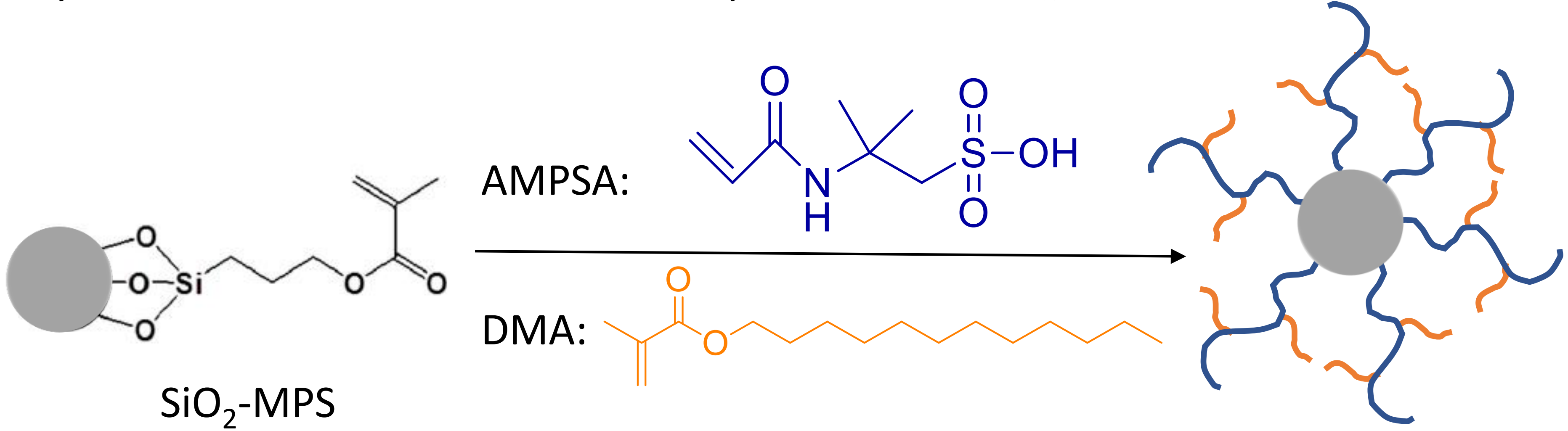
MPS :



3-(methacryloxy)propyltrimethoxysilane

Polymer-coated nanoparticles (PNPs)

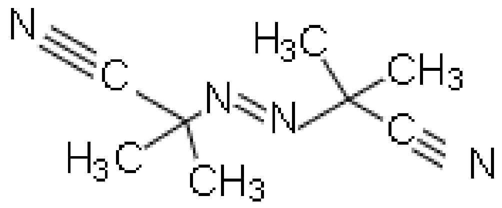
*2) Polymerization of AMPSA and DMA monomers onto the functionalized SiO_2-MPS NPs (**SiO_2-P(AMPSA-co-DMA)**)*



SiO_2-P(AMPSA-co-DMA)

- ✓ dispersed **SiO_2-MPS NPs in DMF** - sonication
- ✓ add **AMPSA** 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

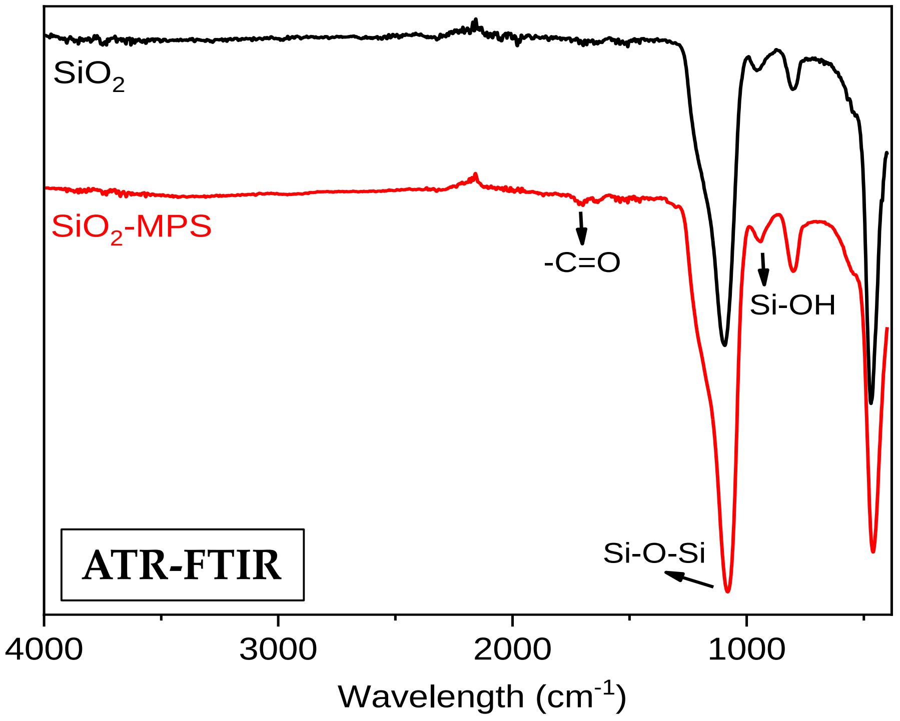
AIBN:

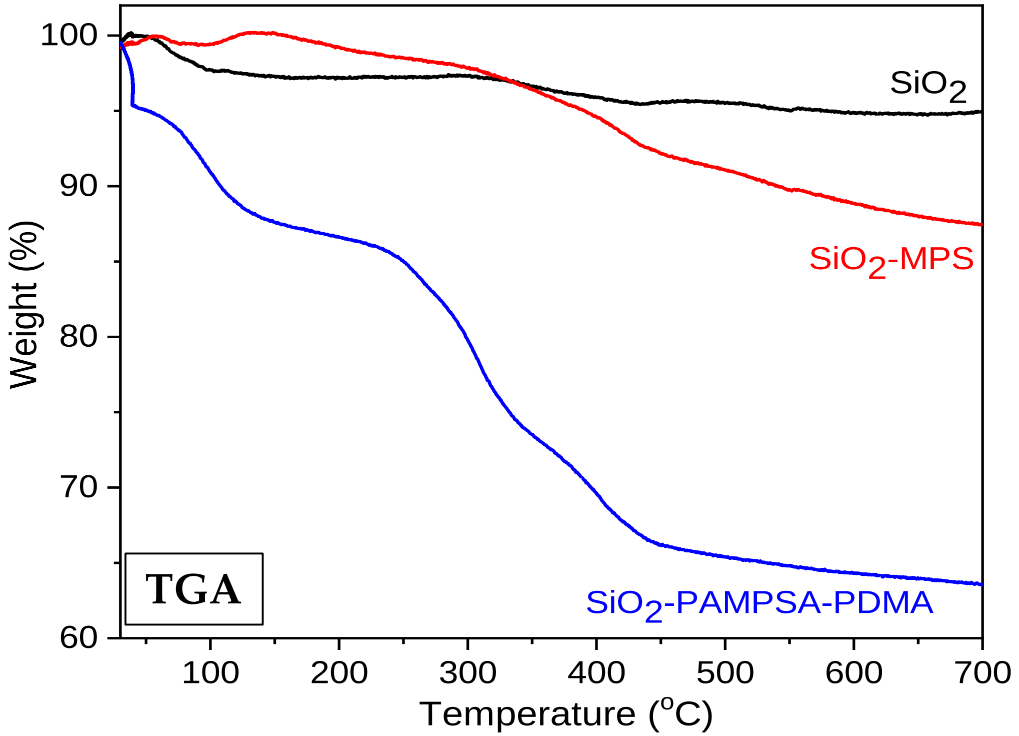


Azobisisobutylronitrile

3rd International Conference on Environmental Design, ICED2022

PNPs Characterization





<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**

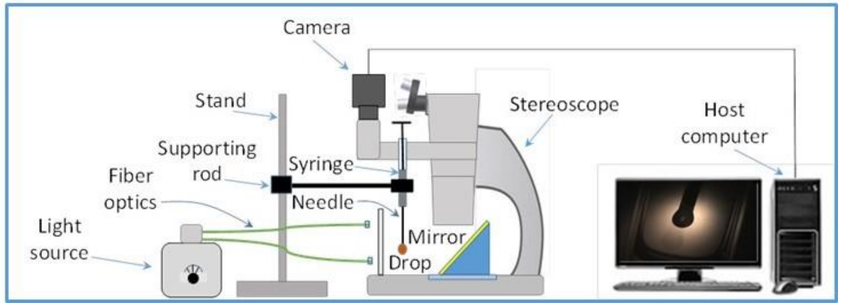
✔ Successful surface modification of the SiO_2 NPs by MPS and at a next step by P(AMPSA-co-DMA)

3rd International Conference on Environmental Design, ICED2022

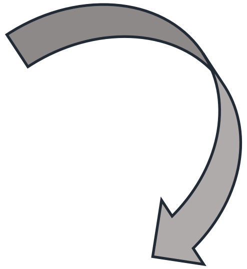
Surface Tension Characterization

Pendant Drop Method:

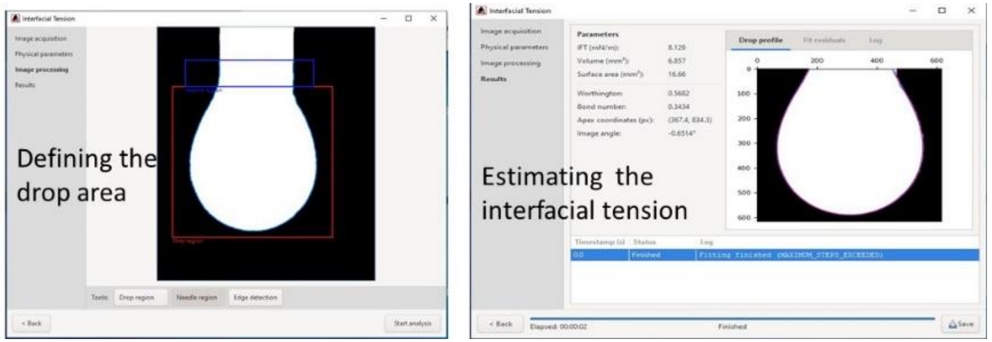
Dynamic Surface and Interfacial Tension of nano-colloid suspensions



Experimental setup of ***pendant drop method***



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

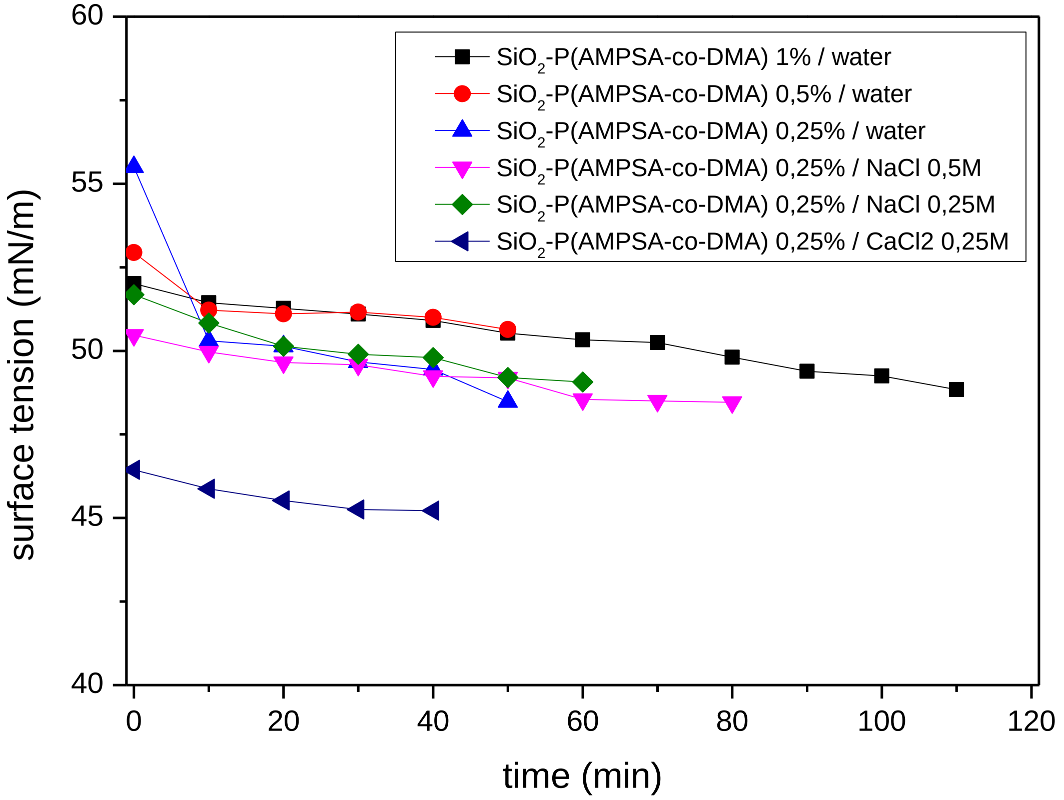


Estimation of surface/interfacial tension by ***OpenDrop software***

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

Surface Tension Characterization

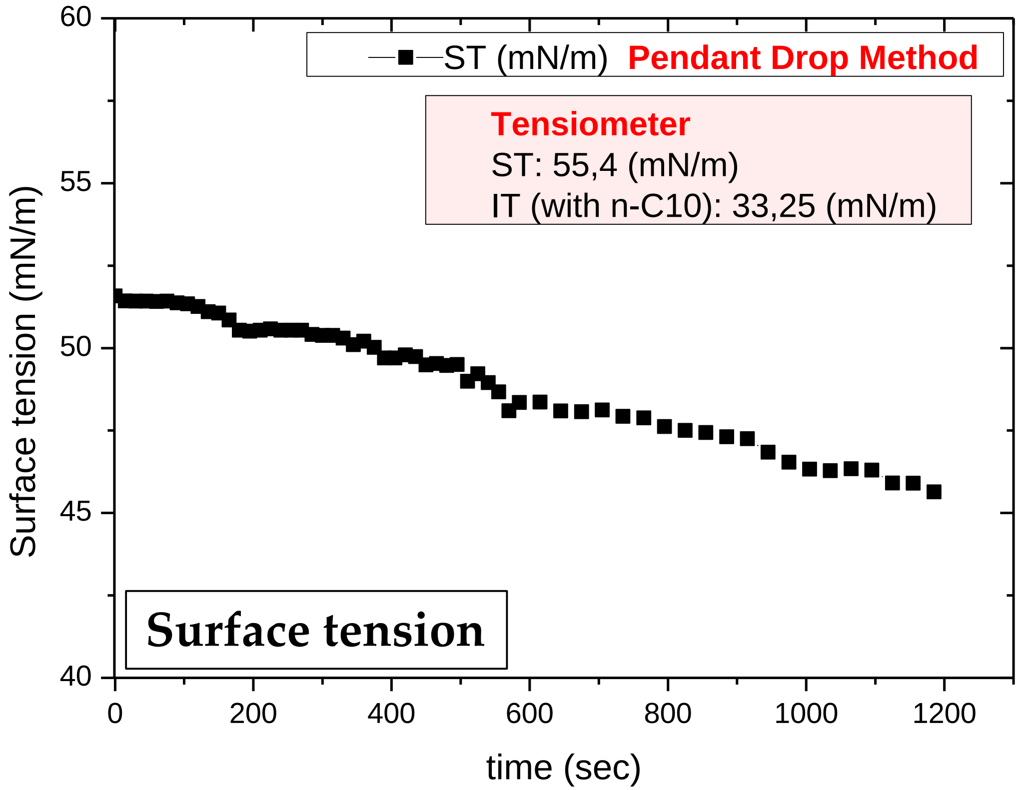
Dynamic surface tension (ST) as function of time for various concentrations of SiO_2-P(AMPSA-co-DMA) NPs in water and salt solutions (NaCl, $CaCl_2$).



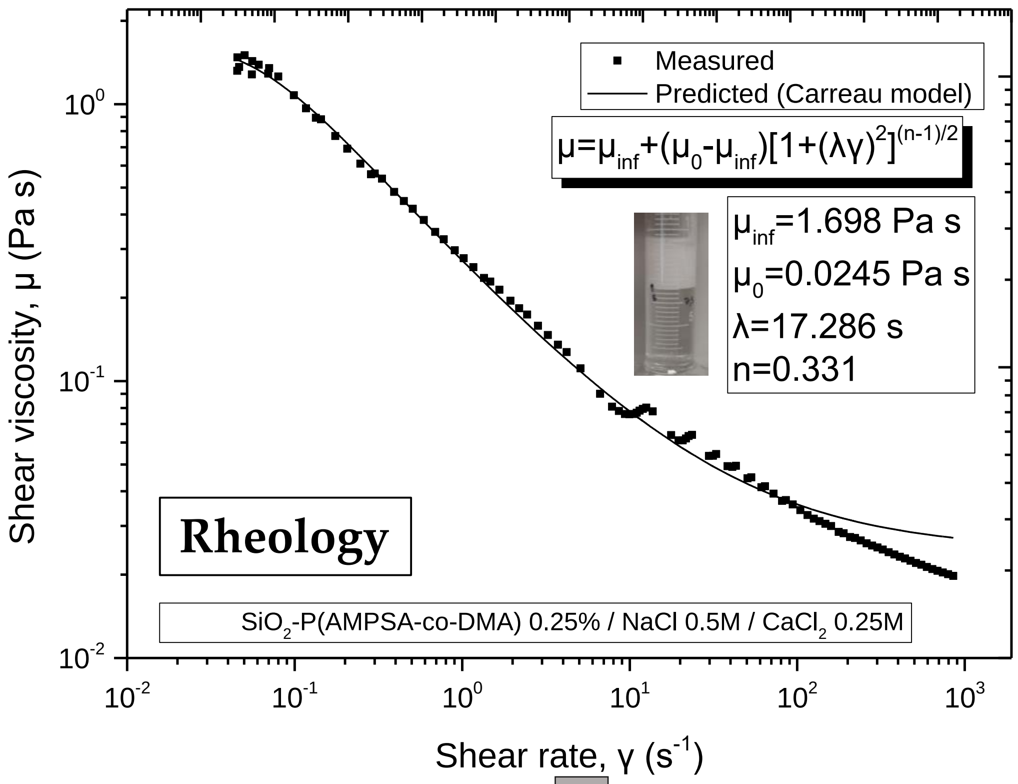
- Maximized reduction rate of ST of SiO_2-P(AMPSA-co-DMA) NPs at PNP concentration equal to 0.25%
- with the addition of NaCl, the ST changes weakly
- with the addition of $CaCl_2$, the ST drops significantly, due to the stronger electrostatic interactions of the divalent $CaCl_2$ with the P(AMPSA-co-DMA)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



respectable reduction rate of ST with time

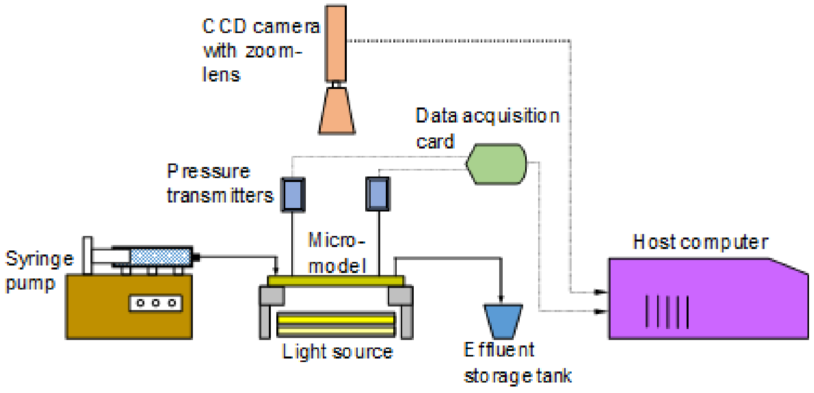


The shear thinning rheology of the Pickering emulsion was fitted satisfactorily with the Carreau model

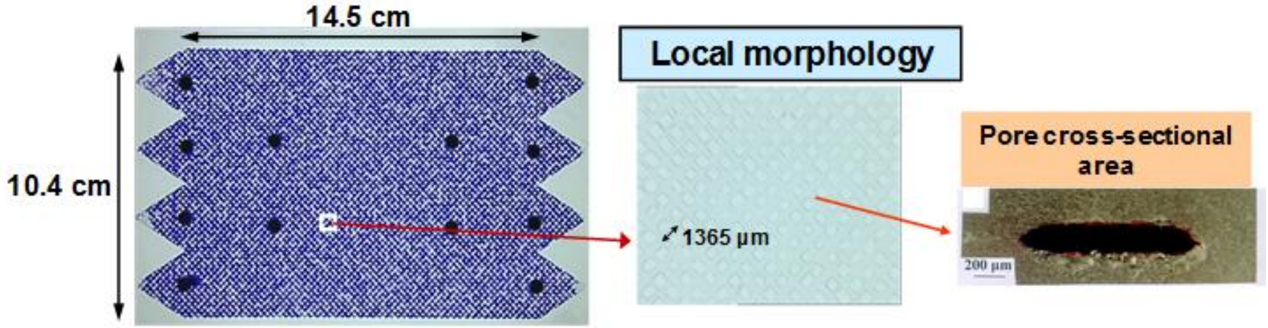
Displacement Test

Visualization EOR tests in a glass-etched pore network

(a) Schematic diagram of experimental setup.



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



Displacement Tests conducted on the glass micromodel

Transient responses of **paraffin oil saturation** for displacement tests,

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

➢ **the PNP dispersion**

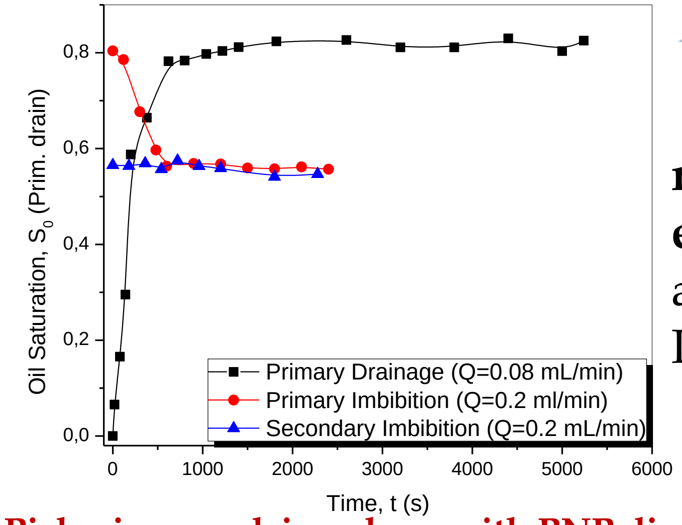
[SiO_2-P(AMPSA-co-DMA) 0.25%/NaCl 0.5M/$CaCl_2$ 0.25M]

or

➢ **Pickering emulsion** along with PNP dispersion

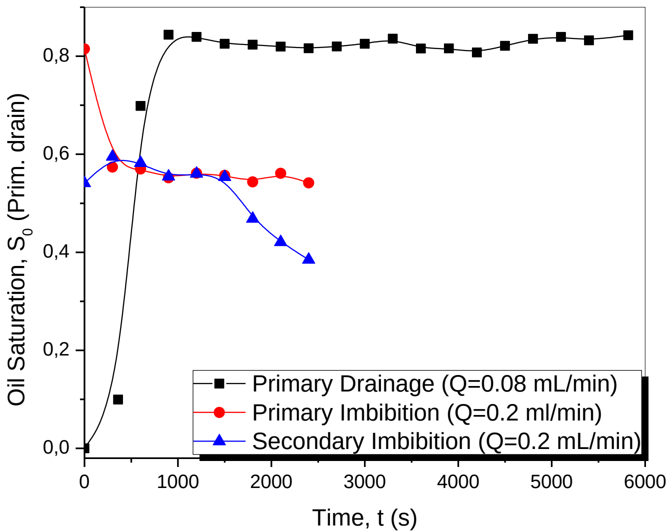
3rd International Conference on Environmental Design, ICED2022

(a) [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

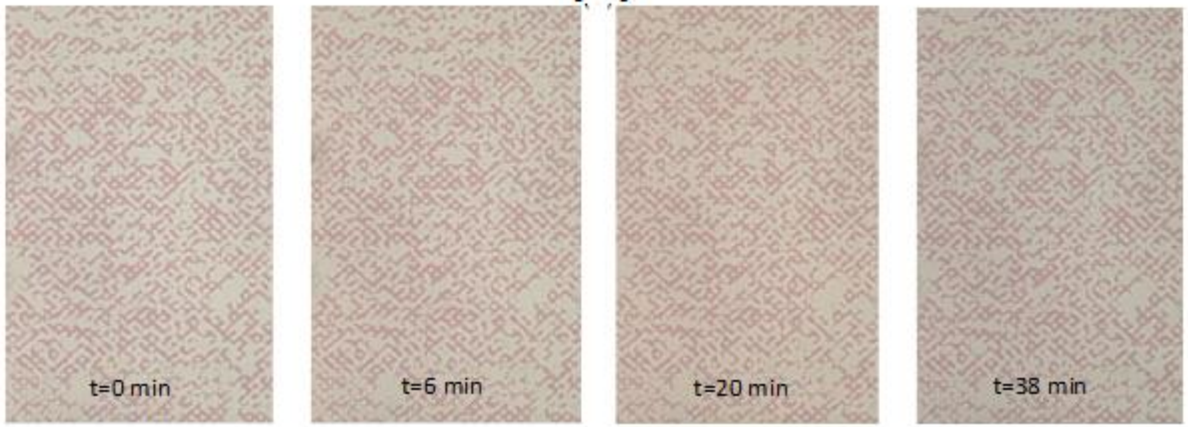
(b) Pickering emulsion along with PNP dispersion



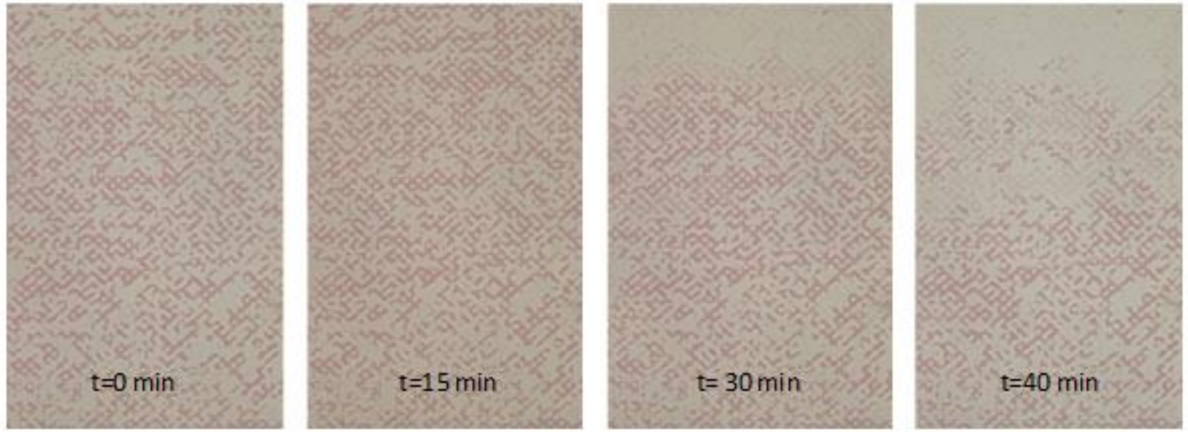
significant EOR efficiency achieved by emulsion and PNP dispersion at equal flow rates

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

(a)



(b)



Displacement tests conducted on the pore network model

Type of displacement	Displaced fluid	Displacing fluid	Flow rate (mL/min)	Injected volume (mL)	Oil saturation	Oil removal efficiency (%)
Drainage	Brine*	Paraffin oil	0.08	8.0	0.825	-
Prim. Imbib.	Resid. paraffin oil	Brine*	0.2	8.0	0.557	32.5
Sec. Imbib.	Resid. paraffin oil	PNP dispersion**	0.2	8.0	0.546	1.97
Drainage	Brine*	Paraffin oil	0.08	8.0	0.843	-
Prim. Imbib.	Resid. paraffin oil	Brine*	0.2	8.0	0.541	35.8
Sec. Imbib.	Resid. paraffin oil	Emulsion***	0.1	4.02	0.385	28.8
		PNP dispersion*	0.1	4.0		

*0.5M NaCl / 0.25M $CaCl_2$; **0.25% SiO_2-P(AMPSA-co-DMA) / 0.5M NaCl / 0.25M $CaCl_2$; ***PNP dispersion / n-C_{10}

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

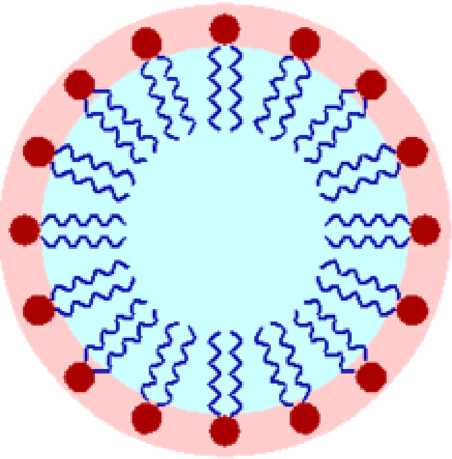
- **Relatively low EOR efficiency** was achieved with the SiO_2-P(AMPSA-co-DMA)0.25% /NaCl 0.5M /$CaCl_2$ 0.25M PNP dispersion

- **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

- *The research project is supported by the Hellenic Foundation for Research and Innovation (H.F.R.I.) under the "1st Call for H.F.R.I. Research Projects to support Faculty members and Researchers and the procurement of high-cost research equipment" (Project Number: HFRI-FM17-361, Title: Enhanced oil recovery by polymer-coated nanoparticles, Acronym: EOR-PNP).*



Thank you for your attention!!!