ISIS@MACH ITALIA

ISIS Neutron and Muon Source

Science and Technology Facilities Council

Experiment Proposal

Experiment number GP2023035

Principal investigator (*)	Dr Eva Santini, National Research Council, ITALY		
Co-investigator			
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Experiment title	Study by Cryo-TEM imaging of the structure of the nanoparticle-surfactant layers stabilizing o/w emulsions		
MRF Instrument	**Cryogenic Electron Microscopy**	**Days requested:**	5
Access Route	Direct Access	**Previous GP Number:**	NO
Science Areas	Materials	**DOI:**	-
Sponsored Grant	Yes	**Sponsor:**	Other
Grant Title	EU MSCA-ITN	**Grant Number:**	-
Start Date	-	**Finish Date:**	-
Similar Submission?	-		
Industrial Links	-		

Non-Technical Abstract

Emulsions are oil-water dispersed systems, which need to the addiction of stabilising agents since they are thermodynamically unstable. The utilisation for this aim of particle-surfactants nanostructures represents a technologic and scientific frontier in the stabilisation of liquid films in emulsions for their exploitation in several applications, from pharmaceutical to the production of porous materials. we propose to use the Cryo-TEM imaging to observe dodecane/water emulsions in the presence of a stabilizing system composed by colloidal silica nanoparticles (SiNP) and a cationic surfactant hexadecyltrimethylammonium bromide (CTAB).

Publications

ISIS neutron and muon source		**IM@IT E-platform:**	No
Instruments		**Days Requested:**	
Access Route		**Previous RB Number:**	
Science Areas		**DOI:**	
Sponsored Grant		**Sponsor:**	
Grant Title		**Grant Number:**	
Start Date		**Finish Date:**	
Similar Submission?			
Industrial Links			

Sample record sheet

Principal contact	Dr Eva Santini, National Research Council, ITALY		
MRF Instrument	**Cryogenic Electron Microscopy**	**Days Requested:** 5	
Special requirements:			

SAMPLE

Material	dodecane/water emulsion in the presence of colloidal silica nanoparticles and a cationic surfactant CTAB (hexadecyltrimethylammonium bromide)	-	-
Formula	-	-	-
Forms	Liquid		
Volume	5 ml		
Weight	mg		
Container or substrate	vials	-	-
Storage Requirements	-	-	-

SAMPLE ENVIROMENT

Temperature Range	- K	-	-
Pressure Range	- mbar	-	-
Magnetic field range	- T	-	-
Standard equipment	Do Not Know	-	-
Special equipment	-	-	-

SAFETY

Prep lab needed	Yes	-	-
Sample Prep Hazards	No	-	-
Special equip. reqs	magnetic stirrer	-	-
Sensitivity to air	No	-	-
Sensitivity to vapour	No	-	-
Experiment Hazards	No	-	-
Equipment Hazards	-	-	-
Biological hazards	No	-	-
Radioactive Hazards	No	-	-
Additional Hazards	-	-	-
Additional Details	-	-	-
Sample will be	Disposed of by instrument scientist	-	-

Science Case

Background and Context

Emulsions are systems of great interest for many applied fields spanning from pharmaceuticals, cosmetics, foods to oil recovery or development of new nano-structured soft materials. Emulsions are water-oil dispersed systems, thermodynamically unstable, which tend to separate under the effect of external forces and/or perturbations. In the last decades, the attention has been focused on the study of complex systems composed by a surfactant adsorbed to nanoparticles (NP) surface as emulsion stabilizers. The interaction between the two components permits to have a mixed NP-surfactant layer at o/w interface which acts as a barrier against the drop coalescence, not only for a steric effect but also changing the viscoelastic properties of the liquid interface.. In particular, cationic cetyltrimethylammonium bromide (CTAB) can adsorb on the negatively charged silica nanoparticles (SiNP), forming partially hydrophobic complexes, able to spontaneously segregate at the aqueous interfaces, modifying their properties (see fig. 1) [1-4]. The observation of the nanoscale structure of these mixed layers for understanding how the layer is arranged is a fundamental issue concerned with the control of the properties of related products, such as the lifetime of the emulsions. Cryogenic Electron Microscopy in Transmission (Cryo-TEM), a method currently used for the study of the morphology of many complex liquids, is characterized by excellent preservation of the original structures [5, 6, 7]. This is made possible by ultra-rapid thermal fixation, i.e. vitrification of the samples, avoiding chemical alteration and physical distortion of the samples.The research program benefits from many years of activity of the proponents (ICMATE-CNR) in surfactant and NP adsorption layers characterization and modelling. The proposer, moreover, participates to funded projects, EU MSCA-ITN project “nanoPaInt - Dynamics of dense nanosuspensions: a pathway to novel functional materials” and Italian Space Agency project “GLAMS - Geopolymers for Lunar Additive Manufacturing and Sensing”, whose research activities are partially pertinent to the topic of the present proposal.

Proposed experiment

The aim of the proposed work is understanding the structure of complex nanoparticle-surfactant layers formed at the liquid-liquid interface, responsible of the stabilization of the water-in-oil emulsion. The high Cryo-TEM imaging potentiality regards the fact that such layers can be investigated at the interfaces of emulsion droplets during ageing. The instrument resolution will allow us to obtain a clear picture of the CTAB+SiNP interaction and their arrangement between dodecane and water. Cryo-TEM images will represent a complementary tool for deepening how an o/w emulsion can enhance its stability against the mechanisms leading to the complete separation of the liquid phases. The proposed system has been already studied from the interfacial properties point of view (i.e., interfacial tension and dilational viscolesticity) by the profile analysis tensiometer technique (PAT-1 Sinterface-Germany), hence some assumptions concerning the adsorption of CTAB molecules onto the SiNP surface and their transfer to the liquid interface have been done (fig.1).

Summary of previous characterisation

Dispersions of colloidal silica nanoparticles with different amount of CTAB have been investigated, in order to understand the particles/fluid interfaces interactions and their effect on both the macroscopic interfacial properties and the corresponding disperse systems. In particular, the studies regarded the water/hexane interface, but similarities have been observed also with dodecane as oil phase. Rheological studies have evidenced the diffusional transfer as an important process at the basis of the transport of nanoparticle to the surface but, with the increasing of the particle surface density, also a reorganisation process at the interface has to be accounted for in order to explain viscoelastic characteristics of the layer. This is corroborated by the observation of the oil droplets behaviour which showed the saturation and the consequent buckling of the interface when subjected to a contraction. The formation of this solid-like layer is also related to the particular morphologies assumed by the oil in water emulsions obtained with the same compositions. For these emulsions, it has been observed an increase of the polydispersity and of the deviation from the sphericity (see fig. 2) while increasing the affinity of nanoparticles for the fluid interface.

Justification of experimental proposals request

The features of Thermo Scientific™ Glacios™ Cryo-TEM guarantee the preservation of the fluid microscopic morphology and the observation of a realistic conformation of the SiNP+CTAB adsorbed layer at the water/dodecane interface surrounding the oily droplets. The emulsions under investigation will be dodecane in water emulsions with 50/50 ratio between the oil and water phases. Dodecane has been chosen because in most real applications, interaction between aliphatic chains of oil and of surfactants is one of the driving forces determining the behaviour of interfaces. Moreover, dodecane has low volatility and we already performed some preliminary experiments. SiNP will be dispersed in the aqueous phase (1%wt) and their complexation with CTAB shall happen in water. The emulsions will be prepared in a 5 ml vial by magnetic stirring at 1000 rpm for 1 hour. The SiNP amount will be kept constant, while the CTAB concentration will range between $5*10^{-5}$M to $8*10^{-4}$M, a maximum of 6 samples in total will be studied. The requested time is 5 days: 1 day for the emulsions preparation and planning of the experiments, 2 days for sample vitrification and 2 days for samples analysis.
Details of the involved materials:
Colloidal SiNP: Surface area (mm^2): BET area 200m^{-2}/g, size 15nm, negatively charged
CTAB (hexadecyltrimethylammonium bromide): cationic surfactant, water soluble, MW 364.45g/mol
Dodecane: hydrocarbon, liquid, $C_{12}H_{26}$

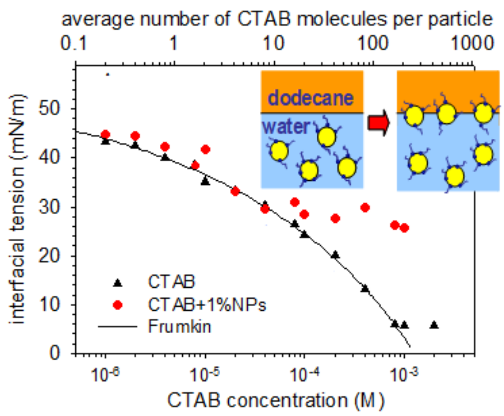

***Figure 1**: Interfacial tension dependence on the surfactant concentration for SiNP-CTAB.*

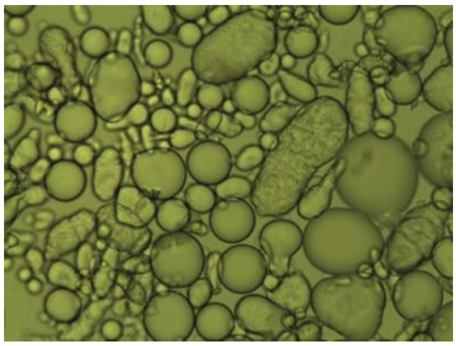

***Figure 2**: o/w emulsion stabilized by SiNP 1wt% and CTAB 10^{-4}M*

References

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