Influence of the Particle Size on Pickering Emulsions Stabilized by Soft and Thermoresponsive Microgels

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Pickering emulsions are surfactant-free metastable dispersions of two non-miscible fluids stabilized by colloidal particles\textsuperscript{1,2}. Such emulsions have been extensively studied over the last two decades using mineral or organic solid particles. More recently, stimuli-responsive microgels have received much attention as stabilizers because of their ability to impart responsiveness to the resulting emulsions. These particles are made of weakly cross-linked polymer swollen by a solvent. Because of their softness, the interfacial behavior of microgels is fundamentally different from that of solid particles\textsuperscript{3}. The aim of the present study is to determine the influence of the microgel size on the emulsion properties.

We used thermo-responsive microgels made of p(N-isopropylacrylamide) as model particles. They were swollen by water below the so-called volume phase transition temperature (VPTT) and shrank above it, due to a change in the polymer/solvent affinity. We varied continuously the stabilizer size and examine the emulsions properties: stability, dispersion state and sensitivity to temperature. We showed that small microgels allow stabilizing very stable and dispersed drops whereas bridging between neighboring drops is obtained for larger microgels. We also showed how these emulsions behave in heating-cooling cycles. We relate the emulsions properties to the microgels structure and deformation at the interface. Microgels are very modulable systems leading to tunable emulsions properties via formulation, chemistry and process path\textsuperscript{3-5}.

Literature:

Kinetics of Evaporation of Droplets: Pure Liquids, Surfactant Solutions, Nanofluids

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We showed that the proportionality of the total evaporation flux to the perimeter of the sessile droplet has nothing to do with the local flux increase in a vicinity of the three phase contact line but is a consequence of properties of governing equations. Computer simulations of the instantaneous flux at evaporation of sessile droplets are carried out in a self-consistent way by considering an interconnected problem of vapour transfer, heat transfer in vapour, liquid and solid substrate, and Marangoni convection inside the liquid droplet [1]. The influence of thermal conductivity of the solid support on the evaporation process is evaluated. We present a theory describing the evaporation of sessile water droplets in presence of contact angle hysteresis [2]. Predicted universal dependences curves are validated against available in the literature experimental data.Experiments on evaporation of sessile droplets of water-based solutions of surfactant SILWET L77 are performed for different ambient temperatures, values of relative air humidity in experimental chamber, and surfactant concentrations. Instantaneous heat and mass fluxes in the system are calculated, giving us the information about the evaporation rate, J, as a function of contact angle, \( \theta \), and contact line radius, L. Based on this dependence we modelled the evolution of the droplet’s shape for two specific modes of evaporation: (I) pinned droplet; and (II) constant receding contact angle. Results of computer simulations are validated against obtained experimental data. It is observed that if surfactant concentration is above the critical aggregation concentration (CAC), i.e. when the surface tension of the solution does not depend on surfactant concentration, then evaporation proceeds in accordance with above described two regimes of evaporation (I) and (II). If the concentration is below CAC, then stage (II) with constant receding contact angle is not observed. Nanofluids are an ever growing topic in modern research due to their unique properties. The influence of nanoparticles have on the wetting properties of fluids has been the subject of increasing interest recently [3]. One of the interesting observations made is that nanoparticles may enhance wetting of a nanosuspension as compared to the pure fluid [4]. However, in spite of the importance the wetting properties of nanofluids to be understood. The influence of nanoparticles on spreading of nanofluids over solid surfaces of variable wettability has been investigated experimentally, using ‘drop shape’ analysis technique. In our studies we used organic (original and modifies polystyrene latex) and inorganic (titanium, silica, carbon) nanoparticles with a range from 10 to 250 nm. We investigated kinetics of spreading of nanosuspensions over surfaces of different hydrophobicity such as silicon wafers, polypropylene, Teflon. Kinetics of spreading of nanosuspensions was investigated using a pure water and solutions of different ionic strength. Our results show that nanoparticles suspended in water has influence of spreading over difference surfaces as compared to the pure water.


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Migration of Flexible Fibers in Poiseuille Flow

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Accumulation is deformable objects, such as vesicles [1] or fibers, in Poiseuille flow at a certain distance from the wall, is a fundamental problem of modern lab-on-chip hydrodynamics. In this work, the dynamics of a non-Brownian flexible fiber in Poiseuille flow between two parallel planar solid walls is investigated theoretically and numerically. A fiber is modeled as a flexible chain of N = 5, 10 or 20 identical, almost touching beads, which interact with each other by elastic and bending forces. The channel width H is much larger than the fiber width d (H=50d) and larger than the fiber length Nd. Initially, the fiber is straight and aligned with the flow at an off-center position, at the distance z₀ from the wall. The characteristic parameters are the ratio k of the Hooke's constant to the hydrodynamic force per bead diameter, and the ratio A of the bending-to-viscous forces. The parameter k is fixed at a very large value, to keep the fiber length approximately constant in time.

The fiber dynamics is evaluated numerically from the Stokes equations, assuming the that fluid sticks to the surface of the fiber and to the walls. The multipole method [2] and the corresponding precise HYDROMULTIPOLE numerical code are used to determine velocity and position of each bead as a function of time. A wide range of the initial positions z₀ across the channel and a wide range of A are considered [3]. Snapshots form the evolution of a fiber are presented in Fig. 1. The main finding is that fibers migrate towards a critical distance from the wall, as shown in Fig. 2. We study how this distance depends on the fiber length N and the bending-to-viscous ratio A [3].

![Fig.1. Snapshot from evolution of a flexible fiber entrained by the Poiseuille flow, for N=20, A=2, z₀=20.](image)

![Fig. 2. Time-dependence of the distance between the wall and the flexible-fiber center-of-mass, for different initial positions [2].](image)

Literature:
Industrial processes involving surfactants vary largely with respect to process conditions such as pH, t, etc. Acquiring information about performance of surfactants used as foaming/defoaming and emulsification/demulsification agents proves to be vital for improving processes. A model system of thin liquid films expressing a behavior correlating to the foam and emulsion properties facilitates the studies of a real system.

Properties of foam films stabilized by polyoxyalkylated diethylenetriamine polymeric surfactants, named A, B, C and D are studied at the pH range from 1 to 12. Surfactant A is an industrially applied agent, while surfactants B, C and D have been recently synthesized. The molecule of each polymer consists of two parts: a more hydrophobic one, where polypropylene oxide (PPO) blocks are predominant and a more hydrophilic one, where polyethylene oxide (PEO) blocks are predominant. Surfactants A, B, and C have a similar structure and belong to the group of the so-called “star-like” polymers, differing only in the number of polymeric branches: 4, 6 and 9 in the mentioned order. Surfactant D is of a dendrites type and its molecule consists of 4 to 6 primary and 2-3 secondary branches.

Dependences of film thickness vs. solution pH (in the range of 6 to 1) and the “isoelectric” points where the value of the diffuse double electric layer potential $\phi_0$ tends to zero are plotted. Results show that the value of the “isoelectric” point as well as the course of film thickness vs. pH dependence is a function of the polymeric surfactant molecular structure.

Studies of film properties vs. pH of the solution in the range of 6 to 12 show that film lifetime increases from a few seconds at pH 6 to more than 5 minutes at pH 12 for one and same surfactant and electrolyte concentration. On the grounds of these results a hypothesis is drawn that with increase in solution pH, the hydrophobic portion of the polymer chain is hydrophylized due to specific hydroxylic ion adsorption; this results in sinking of this hydrophobic portion into the solution which makes the molecular surface area diminish, and hence allows an increase in both surfactant concentration at the surface and the steric disjoining pressure component. (Fig.1). This hypothesis is confirmed by ellipsometric experiments indicating that pH increase leads to increase in adsorption layer thickness at water/air interface.
Aculyn™ 22 and Aculyn™ 33 Polymeric Solutions: Surface and Bulk Rheology and Foaming Properties

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Aculyn™ 22 (A22) and Aculyn™ 33 (A33) are alkali soluble polymer emulsions recommended for applications in cosmetics [1,2]. After dissolution in water at pH 12 both polymers demonstrate a high surface activity.

In this study we explored the possibility of using those polymers as foaming agents and found that the polymeric solutions have very good foamability and form foams stable during the long time. The high stability of foams can be related to the high surface viscoelasticity of solutions under consideration.

Our study has shown that the kinetics of the foam drainage in this case is determined by the solutions bulk rheology, which can be controlled by the concentration of polymer and by the addition of salt, sodium chloride. These parameters affect the surface rheology as well. Both bulk viscosity and the surface viscoelastic modulus increases with the increase of polymer concentration and decreases with the increase of salt concentration. At the same composition, viscosity of A22 solutions is much higher than that of A33 solutions. For the similar bulk viscosity the surface viscoelastic modulus of A33 solutions is several times higher than that of A22 solutions.

Literature:


Acknowledgements:

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Novel Method for Synthesis and Application of Silver Nanoparticles on Wool

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In this study, a new method to obtain antibacterial properties on wool fabric is proposed. First, silver nanoparticles (Ag NPs) were synthesized by a biochemical reduction method. An aqueous solution of extracted dye from \textit{Punica Granatum} bark was used as a reducing agent for synthesis silver nanoparticles from silver nitrate. The nanoparticles formation was followed by UV-Vis absorption spectroscopy (Fig. 1). The size distribution and zeta potential of nanoparticles were evaluated using a particle analyzer (Beckman). The antibacterial potential of biosynthesized silver nanoparticles against E.coli was examined qualitatively and quantitatively. Silver nanoparticles were applied on wool by exhaustion. The amounts of silver deposited on wool fabrics were determined using atomic absorption spectroscopy. The changes in wool fiber surface morphologies after loading of Ag NPs were studied using scanning electron microscopy (Fig. 2) while the elemental composition analysis was done using SEM in Energy-dispersive X-ray (EDX) mode. A series of measurements were carried out to evaluate the effect of Ag NPs on colour of the fabrics under study. The antibacterial efficiencies of treated samples were quantitatively estimated.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Fig_1.png}
\caption{UV-Vis absorption spectra of Ag NPs in aqueous solutions after application of different amounts of reducing agent.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Fig_2.png}
\caption{The SEM image of wool fiber loaded with silver nanoparticles.}
\end{figure}