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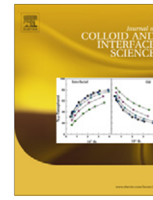

Cleansing dynamics of oily soil using nanofluids

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ABSTRACT

We explored the technological concept of the nanoparticle structuring in the wedge film with regards to its application to the oily soil removal phenomena. The experimental and theoretical investigations on the cleansing of canola oil from a glass substrate using commercially available nanofluids were pursued. Five commercially-available nanofluids with pHs varying from 9.3 to 9.9 were used in the experiments. Experimental results clearly indicated that the time to separate the oily soil from the glass surfaces by nanofluids was much shorter than that for the reference alkaline solution at the same pH. The positive contributions of the nanoparticles to the soil cleaning performance were rationalized in terms of the decrease in the contact angle and the interfacial tension, positive second virial coefficient, and high osmotic pressure of the nanofluid. The effective nanoparticle diameter and the effective volume (i.e., concentration) of the nanoparticles were determined using our novel capillary force balance technique in conjunction with the microinterferometric method. Using the experimentally measured values of the effective particle diameter, effective volume, and the osmotic pressure, the structural disjoining pressure in the wedge film was calculated from a theoretical model based on the statistical mechanics theory. The experimental data for the oil cleaning performance correlated well with the calculated values of the disjoining pressure, the spreading coefficient, and the film tension. We used the drop profile analysis based on the Laplace equation augmented with the extra term of the disjoining pressure to theoretically analyze the nanofluid spreading and wetting phenomena, and the detachment of the oil drop from the solid surface. These results confirm the novel mechanism of detergency using nanofluids based on the normal force (i.e., structural disjoining pressure) arising from the ordered nanoparticle structure formation in the confined space between the soil and the solid substrate (i.e., the wedge film).

1. Introduction

Several mechanisms have been discussed in the literature in relation to the cleaning of solid surfaces with oily deposits [1]. The most common mechanisms discussed are "rolling-up" [2], emulsification [3] and solubilization [4]. Which mechanism prevails depends on the specific soil phase, the solid type, temperature, hardness of the water, electrolyte concentration, and the surfactant type and concentration. It is important to reveal the physicochemical factors that can efficiently control the cleaning process. The type and concentration of the surfactants and electrolytes used can affect the cleansing process by changing the interfacial tension, the three-phase contact angle, and the solubility of the soil in the aqueous phase [5].

The detachment of the soil has also been shown to depend on hydrodynamics. Mahe et al. [6] showed that detachment in the laminar flow regime occurred when a critical shear rate is achieved. This suggests that higher velocities increase the probability of detachment. In addition, the removal of a mobile interface from a solid surface is related to the instabilities that develop when the interface is deformed. Chaterjee [7] used the drop shape analysis to calculate the critical Eotvos number of oil drops detached by buoyancy, but his explanation is not valid when the buoyancy actually prevents the drop's detachment, e.g. a sessile oil droplet on a solid surface. Kolev et al. [8] investigated the detachment of oil drops from a solid surface in a solution of ionic surfactants. A generalized Neumann–Young equation, including a line-drag force (that is proportional to the contact line velocity), was proposed to be valid under the dynamic conditions [9,10]:

$$\beta \frac{dR_c}{dt} = \sigma_{ow} \cos \theta_c^w + \sigma_{ws} - \sigma_{os}. \qquad (1)$$

where σ_{ow}, σ_{ws} and σ_{os} are the interfacial tensions of the oil–water, water–solid, and oil–solid boundaries, respectively. They hypothesize that a line-drag coefficient, β, is a fundamental property of the system necessary to completely specify the problem; the coefficient also needs to be regressed from the experimental observations of the contact line velocity, $\frac{dR_c}{dt}$, and dynamic contact angle, θ_c^w, measurements. Kralchevsky et al. [11] studied the effects of temperature, and the surfactant and salt concentrations on the dynamics of drop detachment. After re-examining the friction coefficient in

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Kolev et al. [8], they found the results could not yield a linear regression in Eq. (1). They modified their understanding and tried to re-introduce the idea concerning water diffusion between the oil and substrate, as originally suggested by Kao et al. [12]. In their analysis, they did not include the role of the micellar interactions in the wedge film (three-phase contact region) on the soil removal.

Most of the data in the literature do not provide a comprehensive basis for understanding the cleansing dynamics. Important details of the washing action of surfactant solutions are not yet well understood. Kao et al. [12] investigated the detachment of crude-oil drops from glass in anionic surfactant solutions and observed the dynamics of penetration of the aqueous-micellar film between the oil phase and the solid. Using the reflected light interference microscopy, Kao et al. studied the profile of a crude oil–water interface and found that there were two distinct contact lines – an outer one (between the oil droplet, solid, and water film) and an inner one (between the oil droplet, solid, and mixed oil–water film). The existence of a mixed oil–water film was thought to be a result of the "diffusion" of the surfactant carrying the aqueous solution into the space between the oil droplet and the solid surface. The experimental observation indicated that the shrinking of the three-phase contact line of solid–oil–water is related to the imbalance of the interfacial tension forces at the three-phase contact line leading to formation of aqueous film containing micelles. Once such a disjoining aqueous film has been formed, even a weak shear flow is able to detach the oil drop from the substrate. Kao et al.'s work revealed that the diffusion of water and the surfactant/micelles between the soil droplet and solid surface is a new mechanism of soil removal.

Wasan and Nikolov [13] further investigated the nature of the interfacial forces that drive the formation of the aqueous film containing nanoparticles resulting in the displacement of the oil droplet from the solid surface. They showed that in the wedge-shaped meniscus geometry, the micelles present in the aqueous medium could be expected to arrange themselves into well-ordered layers (Fig. 1a) [14], the extent of the ordering has the maximum at the vertex of the wedge (where the oil droplet meets the solid surface), and gradually gives way to thermal disorder near the outer end of the wedge. They provided proof of such particle ordering by showing both cubic and hexagonal packing patterns from photographs of 1 μm latex particles in a liquid wedge formed between a glass bubble pressed against a glass surface. It was shown both experimentally [15] and theoretically [16] that nanoparticles (micelles being one example) suspended in a fluid can arrange themselves in layers and even from 2-dimensional layered structures when confined between plane parallel walls, and that such an arrangement results in an excess normal pressure in the film (compared to the bulk liquid) called the structural disjoining pressure (Fig. 1b) [14]. The calculated disjoining pressure oscillates as 1, 2, 3 and 4 layers of hard spheres can be accommodated in the film or meniscus wedge confinement. The calculated spreading coefficient increases with a decrease in the film thickness. Their results indicate that the 2-dimensional in-layer particle structuring can enhance the spreading of nanofluids on solids. This suggests that the driving force for the nanoparticle film self-structuring is due to entropic force [16]. It may be noted that the ingress of the aqueous film into the wedge (Fig. 1a) driven by the structural disjoining pressure gradient (or film tension gradient) is equivalent to the removal of the oily soil droplet from the solid surface – this is a new understanding of the detergency mechanism.

In the above overview of the present understanding of detergency, we see that all the previous models except those of Wasan et al. [13–19] deal exclusively with the role of tangential (interfacial tension) forces and neglect the role of the normal (disjoining pressure) forces on the removal of an oil drop from a solid surface. Further, they ignore the effects of the surfactant micelles' size, concentration, and the soil–solution–solid wedge confinement on soil removal. The goal of this study is to elucidate the effect of the structural force caused by the nanoparticle structure formation in the wedge film on the cleansing phenomena. Wasan and Nikolov [13] proposed that the film tension gradient induced by micellar structuring inside the wedge film removes the soil from the solid surface. In this study, this hypothesis was tested by replacing the surfactant micelles with nanoparticles to induce the film tension to cause the soil removal. We applied the new cleansing mechanism to the cleansing of canola oil using nanofluids containing silica and polymer nanoparticles. The novel microscopic techniques developed in our laboratory were used to directly observe the cleansing dynamics. The cleansing performance of nanofluids, i.e., the time it took for the soil to separate from the glass surface, was determined experimentally. We examined the effect of the pH, nanoparticle concentration, and water hardness on cleansing. The movements of the oil–solid–nanofluid three-phase contact lines were monitored. We quantified the nanoparticle interactions by the second virial coefficient through the measurement of the turbidity and the refractive index of the nanofluid. We observed the nanoparticle layering phenomena in a thin film formed from

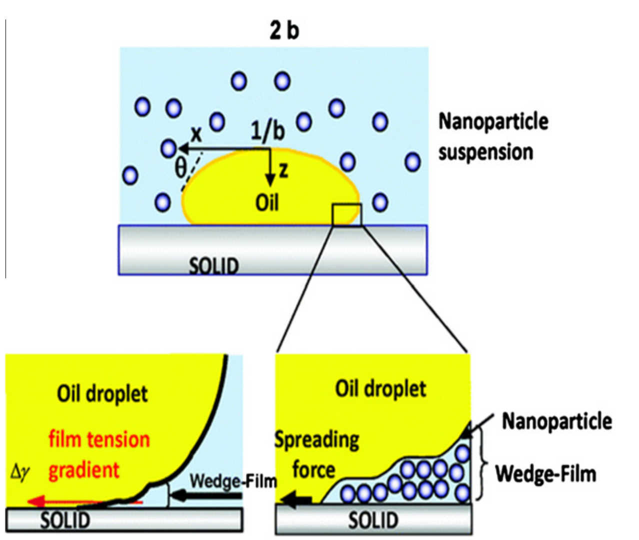

Fig. 1a. Nanoparticle structuring in wedge-film resulting in structural disjoining pressure gradient/film tension gradient at the wedge vertex. [14].

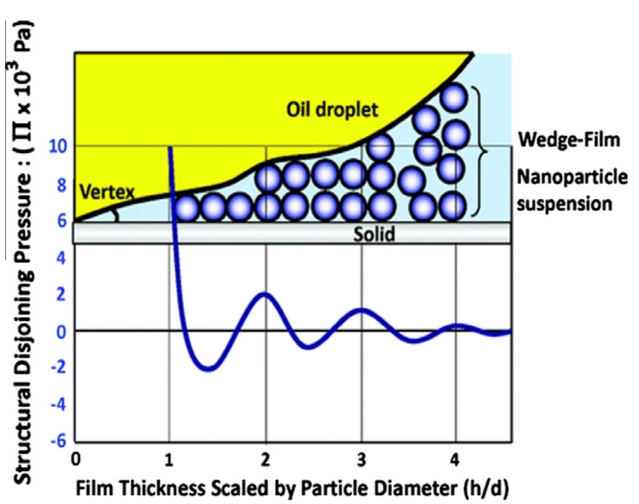

Fig. 1b. Pressure on the walls of wedge for 0.5° contact angle at the vertex as a function of radial distance. Particle volume fraction $\phi = 0.36$ and particle diameter $d = 10$ nm.4. [14].