PHYSICAL REVIEW APPLIED **9,** 034012 (2018)

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Cleaning by Surfactant Gradients: Particulate Removal from Porous Materials and the Significance of Rinsing in Laundry Detergency

Sangwoo Shin,[1,*] Patrick B. Warren,[2,†] and Howard A. Stone[3,‡]

[1]*Department of Mechanical Engineering, University of Hawaii at Manoa, Honolulu, Hawaii 96822, USA*
[2]*Unilever R&D Port Sunlight, Bebington, Wirral CH63 3JW, United Kingdom*
[3]*Department of Mechanical and Aerospace Engineering, Princeton University,*
Princeton, New Jersey 08544, USA

(Received 15 August 2017; revised manuscript received 17 January 2018; published 16 March 2018)

Removing particles from fibrous materials involves loosening via surfactants followed by particle transfer in a flow. While flow advection is commonly believed to be the major driver for pore-scale transport, small pores within the fabric do not allow any significant fluid flow inside them, thus significantly reducing the role of advection. However, rinsing the fabric with fresh water naturally establishes a surfactant gradient within the pore space, providing a suitable environment for particles to undergo diffusiophoresis. We demonstrate that this mechanism can remove particles from deep within fabric pores at an accelerated rate. The nonlinear aspect of diffusiophoresis significantly prolongs the lifetime of the phoretic motion beyond the naive solute diffusion time scale during rinsing, allowing long-lasting, continuous removal of particles. Moreover, owing to the fine balance between chemiphoresis and electrophoresis for particles in anionic surfactant concentration gradients, we show that the particle removal is sensitive to the counterion mobility, suggesting a simple route to control the effect. We thus claim to have resolved the "stagnant core problem"—a long-standing mystery in laundry detergency—and have identified a physicochemical approach to particle transport in fibrous media with broad applicability.

DOI: 10.1103/PhysRevApplied.9.034012

I. INTRODUCTION

Diffusiophoresis, the directed motion of colloidal particles by chemical gradients, was discovered more than seven decades ago [1]. Nevertheless, it has only recently been the subject of renewed interest due to the recognition that the control of chemical gradients makes possible the manipulation of colloidal particles in a wide range of circumstances [2]. For example, diffusiophoresis in salt gradients is highly efficacious at delivering micron-sized particles into dead-end pores, on time scales of minutes rather than the hours that would be required if relying on pure diffusion [3–5]. Electrolyte diffusiophoresis has been implicated as a mechanism for self-propelled "active" colloids [6–8], and in the formation of exclusion zones around ion-exchange resins [9,10]. Similar principles have been applied to design "salt traps" [11] and "solutoinertial beacons" [12]. Diffusiophoresis has been proposed as an inexpensive way to measure zeta potentials [13]; it can be induced by gas dissociation and exploited as a continuous separation process [14]; and in the presence of an opposing flow can lead to rapid pore blocking [15].

Most current research activity has focused on simple electrolyte gradients where significant effects arise from electrophoresis in the diffuse liquid junction potential (LJP) [16]. Very recent interest has developed in ionic surfactants [12,17], but, unlike simple electrolytes, surfactants ipso facto strongly adsorb on particle surfaces and show significant nonideal solution behavior. Therefore, it is not *a priori* obvious that known rules can be generalized to these systems. Also, the surfactant ion mobility is significantly smaller than the counterion mobility so the movement to reduce the free energy of the electrical double layer (chemiphoresis) is typically *opposed* by electrophoresis in the LJP, making the net diffusiophoretic drift magnitude (and even direction) a fine balance between opposing processes.

In this paper, we demonstrate that for anionic surfactants (which are dominantly used in commercial applications) diffusiophoresis nevertheless remains a potent transport mechanism, particularly for cleaning of porous materials such as fabrics. Diffusiophoresis not only results in particles being propelled *down* surfactant concentration gradients, at an accelerated rate, but also provides for a *persistent effect*, similar to the behavior observed for salt traps in simple electrolytes [11]. Our results resolve a decades-old question in laundry detergency concerning the mechanism of particulate soil removal from fibrous

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[*] sangwoos@hawaii.edu
[†] patrick.warren@unilever.com
[‡] hastone@princeton.edu

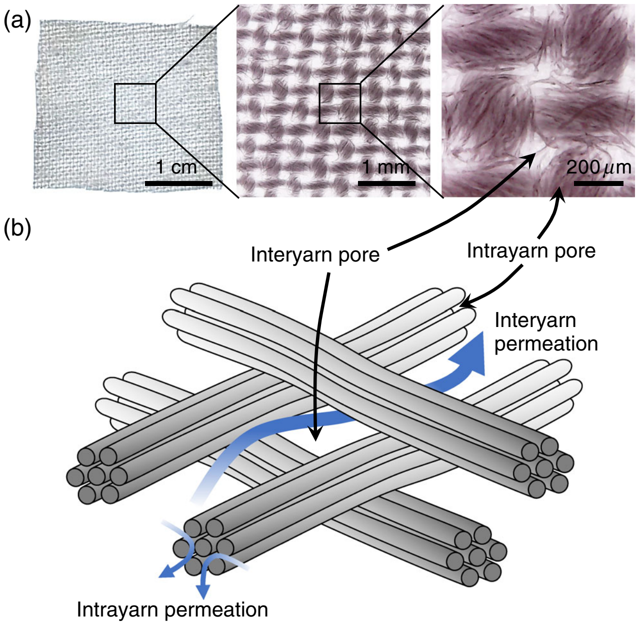

FIG. 1. Biporous structure in fabrics. (a) Micrographs of a typical cotton fabric. (b) Illustration of fluid flow in a biporous fabric. The majority of fluid flow takes place through the larger interyarn pores, whereas only a small fraction of fluid flow can penetrate into the intrapore space.

materials by emphasizing how surfactant gradients established via "rinsing" are important not simply for transporting loose particles but in fact drive diffusiophoresis of soil particles, which allows a strong transport in low-permeability pores in fabrics.

A fabric is a biporous material that typically consists of macroscopic yarns, which are made out of multiple microscopic fibers. Such a structure naturally creates a hierarchical porous geometry where the size of the inter- and intrayarn pores differs by at least an order of magnitude [Fig. 1(a)] [18]. A common understanding in the cleaning of a fabric, which applies to other hierarchical porous materials, is that the soil particles are first detached by the detergent (soil loosening) and then washed away by advection (soil transfer) [18–20]. However, since the length scale of the intrayarn pores is small, advection through the intrayarn pores is hindered significantly. For instance, the Darcy permeability of the interyarn pore region in a common fabric is of the order of 10^{-11} m^2, whereas that of the intrayarn pore region is of the order of 10^{-14} m^2 [18], which implies that 99.9% of the flow goes around the yarns [Fig. 1(b)]. Moreover, the remaining 0.1% of the flow penetrates into the intrayarn pore space only for some extent, resulting in a "stagnant core" inside the yarn where Brownian motion is apparently the only possible transport mechanism [18–20]. A long-standing question has been: How is it possible to remove a significant number of particles from the stagnant core on time scales that are much faster than from pure diffusion out of the intrayarn pore space? One can easily estimate that it should take several hours for micron-sized particles to diffuse out of an order 100-μm-size stagnant core region. Thus, it has long been suspected that some other mechanism must be operative to clean such fibrous materials [19].

During the rinsing process, however, where the fabric that is initially saturated with detergent is exposed to fresh water, the surfactant molecules diffuse out of the stagnant core much more rapidly than do the particles. Although rinsing is primarily intended to discharge excess surfactants and already-removed soil particles present in the bulk solution, we argue here that the transient surfactant gradient established during the rinsing process can provide a pathway for enhanced soil removal from deep fabric pores via diffusiophoresis. In what follows, we demonstrate that diffusiophoresis can take place during the cleaning process of porous materials and present evidence that the surfactant diffusiophoresis is indeed responsible for the missing pore-scale transport mechanism in laundry detergency.

II. RESULTS AND DISCUSSION

As a start, to understand the influence of advection and a surfactant gradient on the particle removal from a deep stagnant core, we use a microfluidic channel where a set of long dead-end pores (width × height × length = $48 \times 10 \times 400$ μm^3) is connected perpendicular to the main flow channel (Fig. 2, see Supplemental Material for details [21]) [4,13]. This geometry represents a condition in which the flow advection is nearly zero, mimicking a stagnant core region. Initially, colloidal particles (polystyrene, diameter $\approx$0.5 μm, zeta potential ≈ -80 mV) suspended in 10 mM sodium dodecyl sulfate (SDS) solution, where 10 mM is the typical upper limit for surfactant concentration in general laundry processes during the wash stage [22], are filled inside the channel including the dead-end pores. Subsequently, the particles are flushed away by the main flow having the same surfactant concentration (10 mM), leaving the particles only in the dead-end pores. Because of the low-Reynolds-number flow near the pore inlet, the main flow can penetrate only to the order of the width of the channel [4,23]. Thus, advection can only remove particles near the pore entrance, implying that the advection alone is ineffective for removing particles from the deep stagnant core region [Fig. 2(a), Movie 1 in the Supplemental Material [21]].

However, lowering the concentration in the main flow to 0.1 mM establishes a surfactant gradient, causing the particles to migrate from the closed pore end by diffusiophoresis [Fig. 2(b), Movie 1 in the Supplemental Material [21]]. This resembles particle transport in dead-end pores in NaCl gradients [3,4]. A significant contribution to diffusiophoresis under these conditions is electrophoresis in the LJP (ϕ_L), which arises because the ions have different mobilities and, in a gradient, a compensating

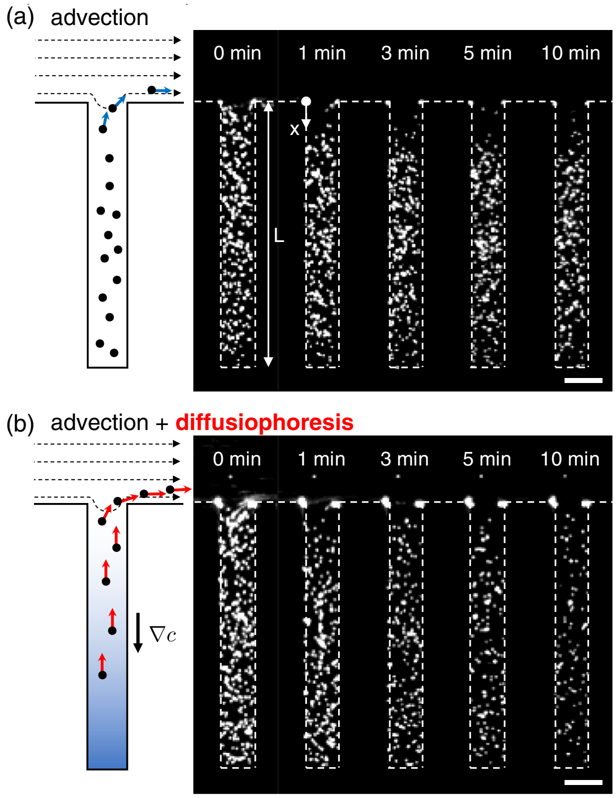

FIG. 2. Particle removal from deep dead-end pores having zero flow advection. (a) Fluorescence image sequence showing particles in the dead-end pore influenced by the advection from the main channel. The solute (SDS) concentration is the same everywhere (10 mM). (b) Image sequence showing particles in the presence of advection and a solute gradient, where the inner (pore) solute concentration is $c_i = 10$ mM and the outer (main channel) concentration is $c_o = 0.1$ mM. All scale bars are 50 μm.

electric field develops until there is no net charge current [16,24]. For SDS, which is a representative model anionic surfactant, the difference in mobilities between the cation (Na^+) and the anion (dodecyl sulfate, DS^-) is relatively large due to the large molecular size of the anion [25]. This feature results in strong electrophoresis driven by the large LJP, since ϕ_L is proportional to the difference in the ion diffusivities normalized by their sum (β), i.e., $\phi_L \sim \beta \equiv (D_+ - D_-)/(D_+ + D_-)$ [26]. We note that the typical diffusiophoretic speed is of the order of 10 $\mu\mathrm{m\,s}^{-1}$ [4,27], which is at least 2 orders of magnitude larger than the typical intrayarn flow speed (order 0.1 $\mu\mathrm{m\,s}^{-1}$) [18,19]; the strong diffusiophoretic motion driven by the SDS gradient allows an effective removal of the particles at an accelerated rate.

SDS not only has a large LJP, but it also has a positive β value ($\beta_{\mathrm{SDS}} = 0.55$) such that negatively charged particles tend to migrate down the SDS gradient [12]. As recently demonstrated by Nery-Azevedo *et al.* [17], SDS strongly adsorbs onto colloidal particles and makes the surface charge highly negative regardless of the particle's intrinsic surface charge, implying that SDS can induce particle diffusiophoresis insensitive to the particle size or surface charge. This feature has an important implication in the cleaning process, where the rinsing of the fabrics with fresh water naturally creates a surfactant gradient such that the negatively charged particles are forced to migrate away from the stagnant core via diffusiophoresis.

Another important aspect of the rinsing process is that the overall surfactant concentration decreases over time. Because the diffusiophoretic velocity $\boldsymbol{u}_{dp} \propto \nabla \ln c$, reducing the overall solute concentration does not necessarily reduce $\boldsymbol{u}_{dp}$ [11,13]. For example, in the case of an SDS gradient with a 100-fold initial concentration difference, particle motion lasts for more than 10 min [Fig. 3(a)], which is much longer than the diffusion time scale (≈4 min for the present setup). In contrast, in the case of NaCl (where the gradient has to be reversed to remove particles [3,4]), despite very strong diffusiophoresis at the start of the experiment, the effect fades on the solute diffusion time scale, leading to an incomplete particle removal [Fig. 3(b)]. The persistent effect for SDS is fundamentally a consequence of the late stage behavior of the surfactant concentration profile which is expected to decay for $t \gg L^2/D_{\mathrm{SDS}}$ as $c(\boldsymbol{r}, t) = f(\boldsymbol{r}) \exp(-\alpha L^2 t/D_{\mathrm{SDS}})$, where the numerical factor $\alpha = O(1)$, D_{SDS} is the surfactant diffusion coefficient, and L the pore length. Under these conditions, $\nabla \ln c$ is time independent. The counterpart phenomenon for NaCl was first reported by Palacci *et al.* [11], who exploited it to make salt traps (i.e., persistent particle capture, rather than persistent particle removal). This result confirms that the use of an anionic surfactant as a diffusiophoretic transport agent leads to long-lasting particle motion, and effectively complete particle removal from deep pores.

Such distinct colloidal dynamics can be modeled by solving an advection-diffusion equation for the particles, where the advection is due to the particle diffusiophoresis induced by surfactant gradients (see Supplemental Material for details [21]) [4,13]. By solving the equation in one dimension, the particle number density (n) and the particle trajectories [gray lines in Figs. 3(c) and 3(d)] can be predicted with reasonable accuracy. A noticeable discrepancy in the experiments is the penetration of the main flow near the pore inlet, which is neglected in the model. We also note a spread of values has been reported for the SDS diffusion coefficient below or near the critical micelle concentration (CMC), ranging from $D_{\mathrm{SDS}} \approx 2 \times 10^{-10}$ to 8×10^{-10} $\mathrm{m^2\,s^{-1}}$ depending on the SDS concentration and the measurement technique [25,28–32]. Because of the competition between chemiphoresis and electrophoresis of particles in SDS solution, the simulated particle diffusiophoresis is highly sensitive to the SDS diffusivity. The best agreement with our data is achieved for $D_{\mathrm{SDS}} \approx 6.0 \times 10^{-10}$ $\mathrm{m^2\,s^{-1}}$, which corresponds to the surfactant monomer diffusivity of $D_{\mathrm{DS^-}} \approx 3.9 \times 10^{-10}$ $\mathrm{m^2\,s^{-1}}$ (see Supplemental Material for details [21]).

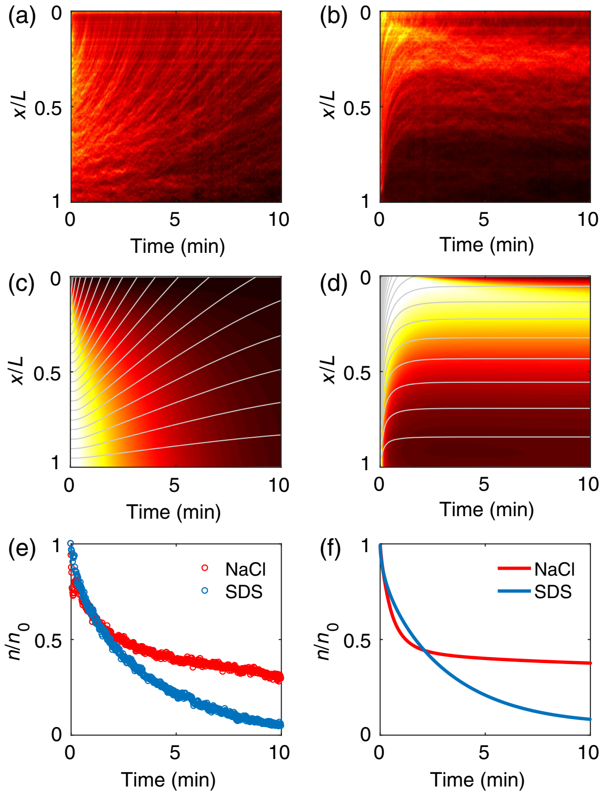

FIG. 3. (a),(b) Experimental and (c),(d) simulation results for the spatiotemporal distribution of particles (polystyrene latex, diameter ≈0.5 μm) under (a),(c) SDS gradient ($c_i = 10$ mM, $c_o = 0.1$ mM) and (b),(d) NaCl gradient ($c_i = 0.1$ mM, $c_o = 10$ mM). Colors in (a)–(d) indicate the experimental fluorescence intensity and the calculated particle number density. The experimental plots are obtained by averaging the fluorescence intensity over the width of the pore. The gray lines in (c),(d) are representative particle trajectories obtained by integrating $\boldsymbol{u}_{dp}$, while neglecting Brownian motion [14]. (e),(f) Particle number density normalized by the value at $t = 0$ s (n/n_0) over time for different solutes (red, NaCl; blue, SDS). The experimental plots in (e) are obtained by counting the number of particles inside the dead-end pore using ImageJ while the simulation plots in (f) are obtained by integrating the particle number density over the entire pore space.

The critical role of the LJP on the particle motion suggests that larger β should lead to more effective removal of particles from the pore. This strategy is demonstrated by choosing various surfactants having the same anion (DS$^-$), but different cations (NH$_4^+$, Li$^+$), as shown in Fig. 4. For example, under the same gradient, ammonium dodecyl sulfate [ADS, Fig. 4(a)] shows much faster particle removal than SDS [Fig. 3(a)] due to the relatively large β value ($\beta = 0.67$) such that most of the particles are removed within 5 min, whereas lithium dodecyl sulfate [LiDS, Fig. 4(b)] shows the slowest and the least effective particle removal among all due to the small β value ($\beta = 0.45$). We note that the average surfactant concentration $c = (c_o + c_i)/2 \approx 5$ mM in the experiments is below the CMC for all of the surfactants [33–35].

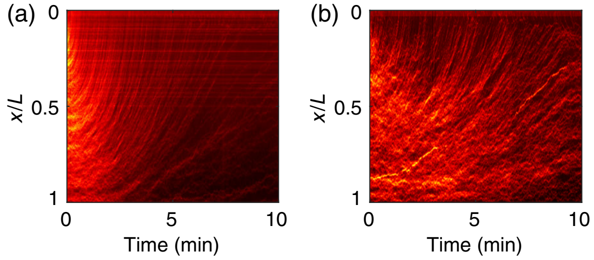

FIG. 4. Impact of β on the particle removal from dead-end pores. (a),(b) Spatiotemporal particle dynamics under (a) ADS ($\beta = 0.67$) and (b) LiDS ($\beta = 0.45$) gradients (both $c_i = 10$ mM, $c_o = 0.1$ mM).

To demonstrate the importance of using fresh water during the rinsing process, we perform model Tergotometer (cleaning) experiments in which we expose a “dirty fabric” that is partially stained with a concentrated colloidal suspension to various solutions (see Supplemental Material for details [21]). The stained fabric is soaked with detergent (10-mM SDS) followed by immersing into either fresh water [Fig. 5(a)] or the same detergent solution [Fig. 5(b)] in a swirling bath (Movie 2 in the Supplemental Material [21]). For comparison, we also conduct the similar experiment with fresh water without introducing any surfactants so that the physicochemical soil loosening step is neglected [Fig. 5(c)]. The first scenario (Fig. 5(a)] renders a common cleaning process including the soil

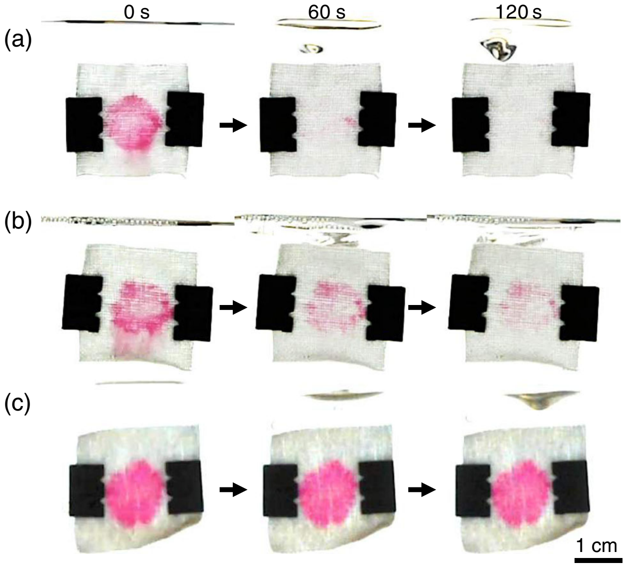

FIG. 5. Rinsing with fresh water enhances the cleaning of fabrics. A piece of fabric (100% cotton) is partially stained with a drop of concentrated colloidal solution (polystyrene latex, diameter ≈0.2 μm) as model soil particles. After drying, the stained fabrics are immersed in either (a),(b) 10-mM SDS solution or (c) fresh water (0-mM SDS). Then, the wet fabrics are placed in a swirling bath with various SDS concentrations; (a) 0 mM, (b) 10 mM, (c) 0 mM.

loosening followed by the soil transfer via both advection and diffusiophoresis, whereas the second [Fig. 5(b)] accounts for soil loosening and advection only, neglecting diffusiophoresis. Obviously, the surfactant is essential for cleaning of the fabric due to the soil loosening; as shown in Fig. 5(c) the particles rarely leave the fabric when the surfactant is absent. In the presence of surfactants, however, rinsing with the fresh water [Fig. 5(a)] further accelerates and enhances the cleaning process compared to rinsing with the waste (surfactant-added) water [Fig. 5(b)] due to the diffusiophoresis driven by the surfactant gradient.

III. CONCLUSION

In summary, we have shown that the efficacy of cleaning fibrous and other porous materials depends on not just the surfactant itself, but also its gradient due to diffusiophoresis. Such surfactant gradients are naturally established during the rinsing process. Thus, rinsing with fresh water is the key to the effective cleaning, as this will maximize the surfactant gradient. We also note that the anionic surfactants enable a long-lasting diffusiophoresis due to their positive β values. This feature allows extending the lifetime of the particle motion out of the deep pores, making fluid flow in large connected channels more effective for transporting particles. We additionally verify a prediction of the theory, that the strength of the effect should be sensitive to counterion mobility, suggesting routes to maximize (or suppress) the effect. Our finding may also shed light on other applications that require the removal of particles and droplets from deep pores through the use of chemical gradients such as chemical flooding for enhanced oil recovery [36].

ACKNOWLEDGMENTS

We thank Orest Shardt for kindly providing the image analysis code and Antonio Perazzo for helpful discussions. We acknowledge Unilever Research and the NSF (CBET-1702693) for support of this research.

P. B. W. discloses a substantive (>$10,000) stock holding in Unilever PLC.

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