

Laundry Detergency of Solid Non-particulate Soil or Waxy Solids: Part I. Relation to Oily Soil Removal Above the Melting Point

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Abstract In this work, methyl palmitate or palmitic acid methyl ester, a monoglyceride, was used as both a model solid fat below the melting point and as an oily soil above the melting point. An anionic extended surfactant [branched alcohol propoxylate sulfate sodium salt ($C_{123}-(PO)_4-SO_4Na$)] was used to remove methyl palmitate from cotton and from polyester. Above the melting point (~ 30 °C) of methyl palmitate, the maximum oily soil removal was found to correspond to the lowest dynamic interfacial tension, as is common with liquid soils. Below the melting point, the lower the contact angle of the wash solution against the soil (indicating higher wettability), the higher the solid fat soil detergency. The removed methyl palmitate was found to be mostly in unsolubilized droplets or particles with a small fraction of micellar solubilization for both solid and liquid forms. The presence of surfactant can prevent the agglomeration of detached methyl palmitate particles in both liquid and solid forms, reducing redeposition and enhancing detergency. Below the melting point, the surfactant aids the solution wetting the surfaces, then penetrating the waxy solid, causing detachment as small particles, and dispersion of these particles. Unlike particulate soil detergency, electrostatic forces are not the dominant factor in fatty soil detergency.

Keywords Solid non-particulate soil · Solid fat soil · Methyl palmitate · Extended surfactant · Laundry detergency

Introduction

In laundry detergency, several factors affect the performance such as the nature of soils, the properties of surfactant, nature of solid surface, mechanical action applied during washing, water hardness, washing temperature, electrolyte level, and additives (e.g., builder, enzyme, and anti-redeposition agent) [1–5]. The previous work on oily soil detergency using different liquid oils demonstrated good correlation between detergency efficiency and interfacial tension (IFT) between the oil and the aqueous solution [6–13]. Recently, our research group has published studies of the mechanisms of particulate soil detergency using carbon black as a model hydrophobic soil and kaolinite and ferric oxide as model hydrophilic soils. It was found that electrostatic forces dominate soil removal, even for nonionic surfactants and hydrophobic fabric [14, 15].

Solid non-particulate soil or solid fat soil is a separate class of contaminants which has properties of liquid and/or solid, depending on temperature. Practical examples of such soils are butter, sebum from human skin, or solidified hamburger or bacon grease. These soils are particularly challenging to remove in low temperature laundry detergency, which is a current topic of great interest due to energy savings and fabric damage at high temperatures. Often, soils are mixtures between liquid and solid fat soils in which the liquid oil is entrapped in the crystal structure of solid oil under a moderate temperature, causing it to be hard to remove. Despite the importance of this soil removal in practical detergency, there are few literature studies of

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solid fat soil detergency. Scheuing [16] studied the detergency mechanism of tristearin (model solid fat soil) using Fourier transform infrared spectroscopy (FT-IR) and reported that the removal of solid triglycerides from a fabric surface was more complex than solid hydrocarbon soils because of the polymorphism in the crystal structure of tristearin. Powe [17] studied detergency of different hydrocarbon soils, and found that the maximum removal of each solid fat soil was somewhere near its melting point. Kawase *et al.* [18, 19] studied the removal mechanism of solid fatty acid soil by using nonionic and anionic surfactants and they reported that solubilization was the dominant mechanism at low temperatures.

An extended surfactant has a group of intermediate polarity, such as polypropylene oxide (PO) or polypropylene–polyethylene oxide (PO–EO) group, inserted between the hydrophilic head and hydrocarbon tail group. As a result of this unique structure, extended surfactants can further extend into both the oil and aqueous phases, resulting in a smoother transition between the hydrophobic and hydrophilic regions at the interface. The presence of a polypropylene oxide group in the hydrocarbon tail of the surfactant molecule helps extend the tail to an oil phase, while still maintaining good interaction with the water phase. Hence, use of an extended surfactant can facilitate the formation of a middle-phase microemulsion, which provides both high solubilization and ultralow interfacial tension (IFT), leading to various applications such as extraction, separation, and textile cleaning [20–23]. Phan *et al.* [24] examined the use of a single extended surfactant in detergency of vegetable oils. High canola oil detergency (>80%) was achieved using a single extended surfactant (C_{14,15}-8PO-SO₄Na) at concentrations as low as 125 ppm and a temperature of 25 °C. Tanthakit *et al.* [8] studied palm oil removal from fabric using microemulsion-based formulations of a mixture of an extended surfactant (C_{14,15}-3PO-SO₄Na) and a nonionic secondary alcohol ethoxylated surfactant [C_{12,14}-O(EO)₅] at a 25:75 weight ratio. The oil removal for this surfactant blend exceeded 90%, which was greater than those of any single surfactant alone and of a commercial liquid laundry detergent. Do *et al.* [25] reported that the mixture of a linear extended surfactant (C₁₀-18PO-2EO-SO₄Na) and a hydrophobic twin-tailed sodium dioctylsulfosuccinate surfactant showed synergism in a Winsor Type III microemulsion formulation, leading to high detergency of vegetable oils and semi-solid fats at low salinity and a low washing temperature.

In this paper, methyl palmitate or palmitic acid methyl ester, a monoglyceride, with a melting point around 30 °C, was used as a model single component solid fat or oily soil being removed from either hydrophilic surface (cotton fabric) or hydrophobic surface (polyester fabric) by using a single anionic extended surfactant at temperatures both

higher and lower than the soil's melting point. Other fundamental physical properties of the system were studied to better understand the forces involved in soil removal and help guide future development of cold water detergent formulations.

Experimental Procedures

Materials

Methyl palmitate or palmitic acid methyl ester (99.8% purity) and Oil red O (solvent Red 27, No. 26125) were supplied by Sigma-Aldrich (BKK, Thailand). Cotton and polyester were purchased from Test fabrics, Inc. (Middlesex, NJ, USA). The surfactant used in this study was an extended surfactant which is a branched alcohol propoxylate sulfate sodium salt with 12–13 carbon numbers with approximately four propylene oxide (PO) units (C_{12,13}-4PO-SO₄Na) with an active content of 30 wt%, as provided by Sasol North America (Lake Charles, LA). Sodium chloride (NaCl), dichloromethane, and isopropanol, all analytical grade, were purchased from LabScan Asia Co., Ltd. De-ionized (DI) water was used to prepare all solutions.

Fabric Pretreatment and Soiling Procedure

Pre-washing of the test fabrics was done using de-ionized (DI) water to eliminate all residues of mill-finishing agents. The pre-washing method followed the ASTM standard guide D4265-98 [26]. After pre-washing, the fabric was cut into 3 × 4 inch swatches in a warp and weft direction. Approximately 0.1 g of the oil-soluble dye was added to 100 mL of the oil above its melting point. The colored oil was filtered until clear. Next, 10 mL of the clear dyed oil was diluted with dichloromethane to 100 mL [27]. The swatches were folded and completely submerged in the diluted dyed oil solution for 5 min. The soiled fabrics were then unfolded and laid on a flat glass plate in a ventilated hood at room temperature (25 °C) overnight in order to dry the soiled swatches. All swatches were freshly prepared for each batch of laundry experiments. By this soiling method, the average weight ratios of oil-to-fabric were approximately 0.20 ± 0.01:1 for the cotton and 0.15 ± 0.01:1 for the polyester.

Laundry Experiments

The laundry experiments were conducted using a tergometer (Copley, DIS 8000), which simulates a home washing-machine action in a bench scale unit. The experimental procedure consisted of a wash step for 20 min with

1000 mL of a surfactant washing solution and two rinse steps for 2 and 3 min with 1000 mL of DI water. An agitation speed for each step was fixed at 120 rpm. Three soiled swatches and one unsoiled swatch for anti-redeposition testing were washed in each bucket for one cycle for replication.

Oil Removal Measurement

Oil removal was quantified based on residual oil on the swatches after washing. The residual oil was extracted by submerging a swatch in isopropanol for 24 h at room temperature, and then the extracted solution was analyzed by an ultraviolet/visible spectrophotometer (Hewlett-Packard, 8452A) [9, 27]. The oil removal was calculated by subtracting the remaining oil residue after washing from the original oil content in each swatch.

Surface Tension Measurements

The surface tension of a surfactant solution with varying surfactant and NaCl concentrations was measured by a Wilhelmy plate tensiometer (Krüss, K100) at two different temperatures (25 and 35 °C). The inflection point of the plot of surface tension versus the log of initial surfactant concentration was used to determine the critical micelle concentration (CMC) [28].

Particle Size Measurement

The particle size distribution of methyl palmitate particles suspended in the washing solution after the wash step at 20 °C was measured by a particle size analyzer (Malvern, Mastersizer X).

Contact Angle Measurement

A 2- μ L drop of a surfactant solution with different NaCl concentrations and two surfactant concentrations of 0.1 and 0.3 wt% was placed on the methyl palmitate surface by using a micro-syringe and the contact angle was measured after 30 s by a contact angle measuring instrument (Krüss, DSA 10 Mk2) using the sessile drop technique. During the measurement, the sample chamber was kept at 25 °C in order to prevent melting of the sample (methyl palmitate).

Oil Solubilization Measurement

An excess amount of methyl palmitate was added to a surfactant solution having a surfactant concentration of 1000 mg/L (10 times CMC) with 5 wt% NaCl or a surfactant concentration of 3000 mg/L (30 times CMC) with 1

or 5 wt% NaCl at different temperatures. The solution was stirred at 120 rpm for 20 min. The surfactant solution phase of the mixture was filtered and the filtrate was measured for total carbon concentration of the dissolved methyl palmitate plus the surfactant by a total organic carbon analyzer (TOC) (Shimadzu, TOC 5000). The TOC concentration of dissolved methyl palmitate was obtained by subtracting the total TOC value with the TOC value of surfactant. The solubility of methyl palmitate obtained was then subtracted from the oil removal to determine the portion of unsolubilized (dispersed or emulsified) methyl palmitate. The measurement time of 20 min was selected to be the same as the wash step time used in the washing experiments. In addition, the oil solubilization measurement was also carried out with varying time until each system reached a maximum or equilibrium solubilization level which was found at around 24 h for all studied systems.

Interfacial Tension Measurement

The measurement of dynamic interfacial tension (IFT) between the aqueous phase (the surfactant solution) and the oil phase (methyl palmitate) for varying surfactant concentrations and temperatures (higher than the melting point of methyl palmitate) was conducted using a spinning drop tensiometer (University of Texas, Model 500). A volume of 1–3 μ L of methyl palmitate (above the melting point) was injected into a 300- μ L capillary tube filled up with a surfactant solution having different NaCl concentrations and two surfactant concentrations of 0.1 and 0.3 wt%. The diameter of the oil drop was recorded 20 min after injection, which corresponded to the time used for the wash step in detergency experiments.

Dispersion Stability Measurement

The dispersion stability of methyl palmitate solid particles having average diameters of 100 μ m suspending in DI water or an aqueous solution containing 0.1 or 0.3 wt% surfactant with different NaCl concentrations at 25 °C (below the melting point) was determined by measuring absorbance as a function of time using a UV–visible spectrophotometer (Hewlett-Packard, 8452A). The solution was prepared by adding the methyl palmitate particles in the surfactant solution, after being well mixed; the prepared solution was transferred to a spectrophotometer cuvette. The reading of absorbance at a wavelength of 550 nm was recorded every 10 s for 2 h. The absorbance values in the range of 2000–5000 s were averaged to represent the dispersion stability. The higher the absorbance, the higher the dispersion stability.

PZC Measurement

A powder sample of methyl palmitate or cotton or polyester fabric was added to distilled water at different solution pH values using a 0.1 M HCl or 0.1 M NaOH solution for pH adjustment. After that, the solution with any added powder sample was kept at 20 °C for 24 h. The initial pH value of this solution, prior to adding the powder sample, and the final pH after 24 h were measured by a pH meter (Ultra basic DENVER Instrument). The point of the intersection of the initial and the final pH lines was used to indicate the point of zero charge (PZC) of each material.

Zeta Potential Measurement

About 3.5 mg of methyl palmitate powder was added into a solution having 0.1 wt% surfactant and different NaCl concentrations. The mixture was stirred and kept at 20 °C for 24 h. Subsequently, the solution was transferred to an electrophoretic cell of a zeta meter (Zeta-Meter 3.0+) equipped with a microscope module. After applying a suitable voltage, the charged particles moved towards the electrode having opposite charge until attaining a steady state (the particles moved with a constant velocity). The velocities were measured and averaged and referred to as electrophoretic mobility which was calculated by the zeta meter instrument automatically [29].

Results and Discussion

Detergency Performance: Optimum Concentrations of Surfactant and NaCl

As shown in Table 1, added surfactant or NaCl has a negligible effect on the melting point of methyl palmitate (we use 30 °C throughout this paper). Figure 1 shows the oil removal and oil redeposition as a function of surfactant concentration and salinity for cotton and polyester at 35 and 25 °C in which methyl palmitate is in

Table 1 Melting point of methyl palmitate in various washing solutions

Solution	Melting point (°C)
De-ionized water	29.5–30.4
0.1 wt% C _{12,13} (PO) ₄ SO ₄ Na	28.5–30.1
0.1 wt% C _{12,13} (PO) ₄ SO ₄ Na/1 wt% NaCl	28.2–30.3
0.1 wt% C _{12,13} (PO) ₄ SO ₄ Na/3 wt% NaCl	29.5–30.3
0.1 wt% C _{12,13} (PO) ₄ SO ₄ Na/5 wt% NaCl	28.0–30.4
0.1 wt% C _{12,13} (PO) ₄ SO ₄ Na/7 wt% NaCl	29.5–30.2

a liquid form and solid form, respectively. At 35 °C, for any given NaCl concentration, with increasing surfactant concentration, the oil removal increased and leveled off for both test fabrics. For any given surfactant concentration, the oil removal reaches a maximum at 5 wt% NaCl as shown in Fig. 1a-1, b-1. At 25 °C, the oil removal gradually increases with increasing surfactant concentration and the oil removal reaches a maximum at 1 wt% NaCl as shown in Fig. 1c-1, d-1. In this work, the ability of low extended surfactant concentration to achieve good detergency is consistent with results of previous studies [23, 24].

Figure 1 also shows the effects of salinity and surfactant concentration on the oil redeposition on cotton and polyester at 35 and 25 °C. The amount of oil redepositing on both fabrics decreased with increasing surfactant concentration and leveled off at a high surfactant concentration, depending on the concentration of added NaCl. For any fixed surfactant concentration, the oil redeposition reached a minimum value at 5 and 1 wt% NaCl at 35 and 25 °C, respectively. The maximum oil removal with the lowest oil redeposition was found at the same surfactant concentration and salinity for both fabrics types and for both washing temperatures.

CMC Results

The CMC values of the extended surfactant with different NaCl concentrations at 25 and 35 °C are shown in Fig. 2a. Increasing electrolyte NaCl concentration causes the CMC to decrease due to decrease of the absolute value of the electrical potential at the micelle surface and lower electrostatic repulsion between surfactant head groups at the micelle surface [20, 23]. Moreover, the CMC values were relatively independent of temperature (those at 25 °C were slightly higher than those at 35 °C for all NaCl concentrations), consistent with low temperature dependence of CMC on temperature for anionic surfactants [30]. The CMC data from Fig. 2a are plotted as the logarithm of critical micelle concentration versus logarithm of total concentration of counterion in the solution at the CMC (from added NaCl and surfactant) as shown in Fig. 2b. This log–log plot is linear and known as the Corrin–Harkins plot [31]. The absolute value of the slope from these plots is the fractional counterion binding to micelles and at 25 °C is 0.29 and at 35 °C is 0.30. These values are only about half of those measured for other ionic surfactants [32, 33], so extended surfactants show unusual electrostatic properties, probably having to do with the packing of the head groups at the micelle surface. In common with other ionic surfactants, fractional counterion binding on micelles has only slight temperature dependence.

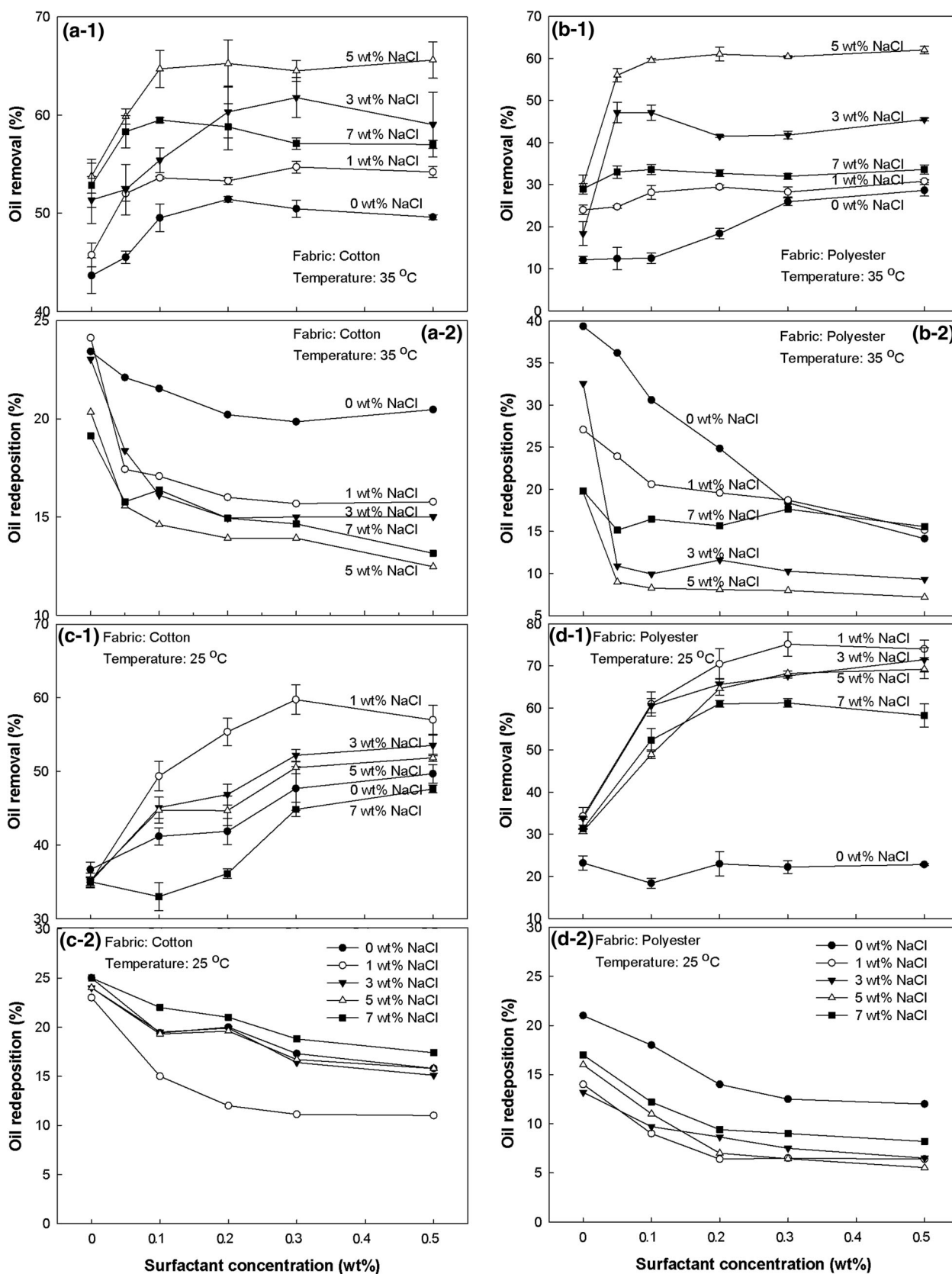


Fig. 1 Oil removal and redeposition of methyl palmitate as a function of surfactant concentration and salinity on both test fabrics **a-1, a-2** for cotton at 35 °C, **b-1, b-2** for polyester at 35 °C, **c-1, c-2** for cotton at 25 °C, **d-1, d-2** for polyester at 25 °C

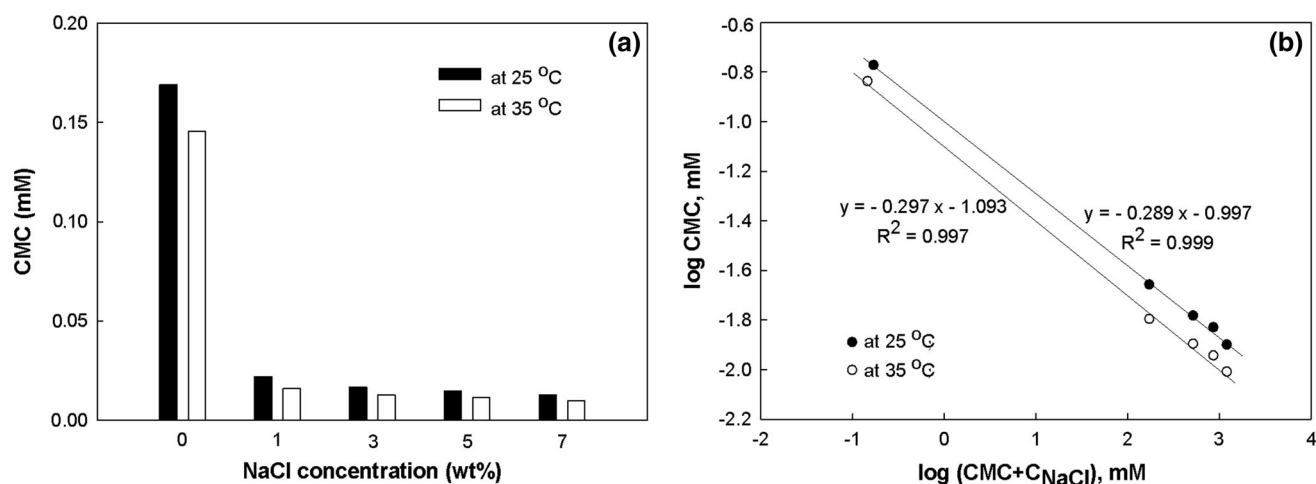


Fig. 2 a Critical micelle concentration (CMC) of $C_{12,13}(PO)_4SO_4Na$ at 25 and 35 °C and b Corrin and Harkins plot of $C_{12,13}(PO)_4SO_4Na$ from CMC data at 25 and 35 °C

Interfacial Tension (IFT) Results

Figure 3 shows the IFT at the interface of the liquid methyl palmitate and surfactant solution as a function of salinity for two surfactant concentrations of 0.1 and 0.3 wt% at 35 °C. The IFT values of the surfactant solution and the liquid oil were measured at 20 min, which is long enough for equilibration [34] and corresponds to the wash step time used in the washing experiments. For both studied surfactant concentrations, all of the surfactant solution–oil IFT values measured (0.0172–0.2773 mN/m) are considered to be in the low and ultralow ranges, except at 0 wt% NaCl (2.39 mN/m) which agree well with the measured IFT values between an extended surfactant and canola oil [24, 34, 35]. All of the measured IFT values were much lower than the deionized water–oil IFT value (7.86 mN/m) and the 5 wt% NaCl deionized water–oil IFT value (7.29 mN/m).

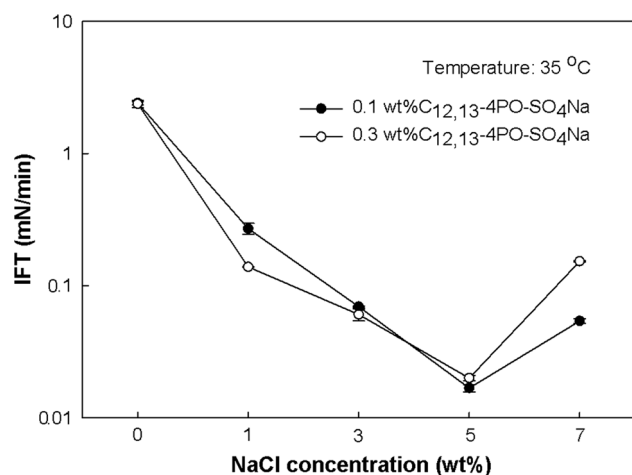


Fig. 3 The correlation of equilibrium IFT using 0.1 and 0.3 wt% $C_{12,13}(PO)_4SO_4Na$ as a function of salinity at 35 °C

Contact Angle Results

The contact angle is a physical parameter indicative of how well an applied solution wets a surface. The wetting is a first step of the complex process of detergency. Figure 4 shows the contact angles of both 0.1 and 0.3 wt% surfactant solutions on the solid surface of methyl palmitate as a function of NaCl concentration at 25 °C. The contact angle decreases with increasing NaCl concentration and reaches a minimum value (indicating maximum wettability) at a NaCl concentration of 5 and 1 wt% for 0.1 and 0.3 wt% surfactant concentrations, respectively. An increase in surfactant concentration from 0.1 to 0.3 wt% could reduce the optimum NaCl concentration studied for detergency performance from 5 to 1 wt%. This surfactant concentration increase to 0.3 wt% also resulted in a decreased contact angle from 38° to 33° at 5 and 1 wt% NaCl,

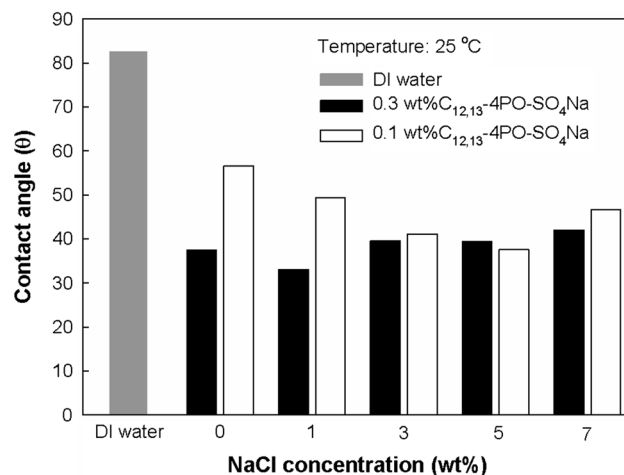


Fig. 4 Contact angle of 0.1 and 0.3 wt% surfactant solution on methyl palmitate surface at 25 °C as a function of salinity

respectively. So, wettability may be a factor in detergency and the simple contact angle measurement may be predictive of cleaning efficiency which would be helpful in formulation development.

Effects of Fabric Type and Washing Temperature on Detergency Performance

Figure 5 shows the effect of washing temperature on oil removal and oil redeposition for polyester and cotton fabrics in surfactant solutions of 0.3 wt% $C_{12,13}(PO)_4SO_4Na$ with 1 and 5 wt% NaCl concentrations and of 0.1 wt% $C_{12,13}(PO)_4SO_4Na$ with 5 wt% NaCl concentration. The washing temperature range of 15–50 °C was studied in order to cover both solid and liquid states of methyl palmitate (melting point of 30 °C). The oil removal increased with increasing wash temperature for both studied fabrics using the washing solution containing 0.3 and 0.1 wt% surfactant with 5 wt% NaCl concentrations. The detergency performance on the cotton was slightly higher than that on the polyester fabric for any wash temperature. For the washing solution having 0.3 wt% surfactant and 1 wt% NaCl, the detergency performance on the cotton fabric reached a maximum level around the soil melting point (30 °C), but did not change substantially with temperature above the melting point. For polyester fabric with the washing solution of 0.3 wt% surfactant and 1 wt% NaCl, the oil removal increased with increasing washing temperature from 15 to 25 °C. However, detergency decreased dramatically as temperature increased further from 25 to 30 °C. After reaching this minimum oil removal at the melting point, detergency slightly increased as temperature increased further beyond the melting point. This somewhat surprising minimum in detergency is confirmed by photographs of washed polyester at different washing temperatures as shown in Fig. 6.

For all surfactant systems on cotton and two of the three systems on polyester, oil removal generally increases with increasing temperature which is generally true in detergency of different soils. However, this temperature inversion effect has been previously observed on hydrophobic fabric. Morris and Prato [3] found that the best removal of particulate and oily soil from cotton fabric was at high temperatures, whereas the nonpolar fraction of oily soil removed from polyester was better at low wash temperature. Illman *et al.* [36] and Gordon *et al.* [37] found that nonpolar sebum was more easily removed from Dacron or Nylon in cold water than hot water. This was attributed to the diffusion of liquid oil into the interior of polyester at high temperatures, causing the oil to have poor contact with the surfactant solution [38].

In our study, the soil was dissolved in a volatile solvent, the fabric immersed in the solvent/soil mixture, then the

solvent evaporated at 25 °C, below the oil melting point. So, when the soil was deposited on the fabric upon evaporation of the solvent, it was a solid. It was suspected that this solid did not incorporate itself into the fabric fibers as a liquid soil would. So, in separate experiments, after the soiling procedure, each fabric was heated up to 40 °C so the soil became liquefied and could diffuse/imbibe into the fabric weave, then cooled to the temperature of the detergent experiment. As shown in Table 2, below the melting point, the oil removal was lower than with normal soiling procedures but at a high wash temperature, detergency was increased around 10%. We conclude that if the soil is a liquid without solvent and allowed to contact the hydrophobic fabric before the system is cooled, as would be the case with sebum and warm hamburger/bacon grease, below the melting point, it is much more difficult to remove the soil than if the soil only contacts the fabric as a solid below the melting point. That this effect is only observed on hydrophobic polyester fabric and not on cotton indicates that the hydrophobic monoglyceride soil has a much stronger attractive interaction with the hydrophobic fabric than a hydrophilic fabric. A broader range of soil polarities would need to be studied to determine the generality of this effect and if monoglycerides/triglycerides are peculiar in their interaction with polyester compared to say hydrocarbon soils. And the temperature inversion effect is not observed for every surfactant system (one out of three here). So, it is recommended that a systematic soiling procedure be used for studies of waxy solids when temperature ranges below the melting point are included.

In a comparison of the two NaCl concentrations in the 0.3 wt% surfactant solution (Fig. 5), for any studied fabric, the detergency performance at 5 wt% NaCl was higher than that at 1 wt% NaCl at a washing temperature above the melting point due to the low IFT values of 0.009–0.09 mN/m at 5 wt% NaCl as compared to those of around 0.1 mN/m at 1 wt% NaCl (Fig. 3). In contrast, for any washing temperature below the melting point of 30 °C, the oil removal at 5 wt% NaCl was lower than that at 1 wt% NaCl, especially on the polyester fabric. The oil removal on the cotton fabric was higher than that on the polyester fabric under studied conditions except at washing temperatures below the melting point with the NaCl concentration of 1 wt%. There is apparently a high affinity of the liquid methyl palmitate and hydrophobic polyester as compared to that on the hydrophilic cotton fabric. However, at a temperature lower than the melting point, the oil removal for the polyester fabric was much higher than that on the cotton fabric, suggesting that the contact of the solid methyl palmitate with the fabric is less than for liquid methyl palmitate. This supports the same conclusion reached from different soiling procedures about solid soil not interacting well with polyester.

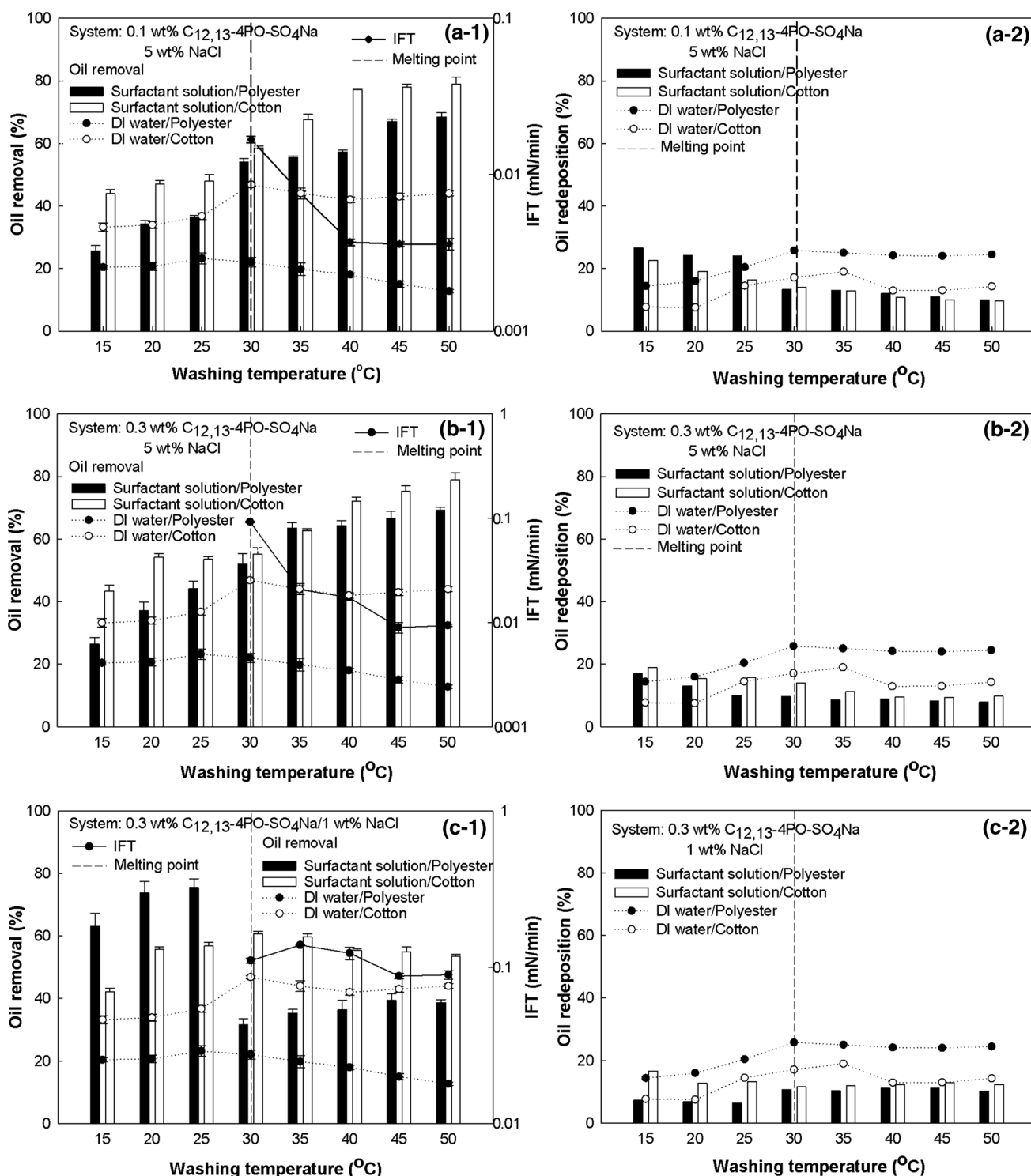


Fig. 5 Oil removal and redeposition as a function of washing temperature in relation to equilibrium IFT at **a** 0.1 wt% C_{12,13}(PO)₄SO₄Na with 5 wt% NaCl, **b** 0.3 wt% C_{12,13}(PO)₄SO₄Na with 5 wt%

NaCl, and **c** 0.3 wt% C_{12,13}(PO)₄SO₄Na with 1 wt% NaCl on both test fabrics of cotton and polyester

The use of surfactant showed a much higher oil removal at any washing temperature as compared to DI water. For DI water systems, the oil removal slightly increased and reached a maximum level at about the melting point for

both test fabrics. Beyond the melting point (30 °C), the oil removal on polyester fabric slightly decreased with further increasing washing temperature. Therefore, the best conditions found at any temperature below the melting point

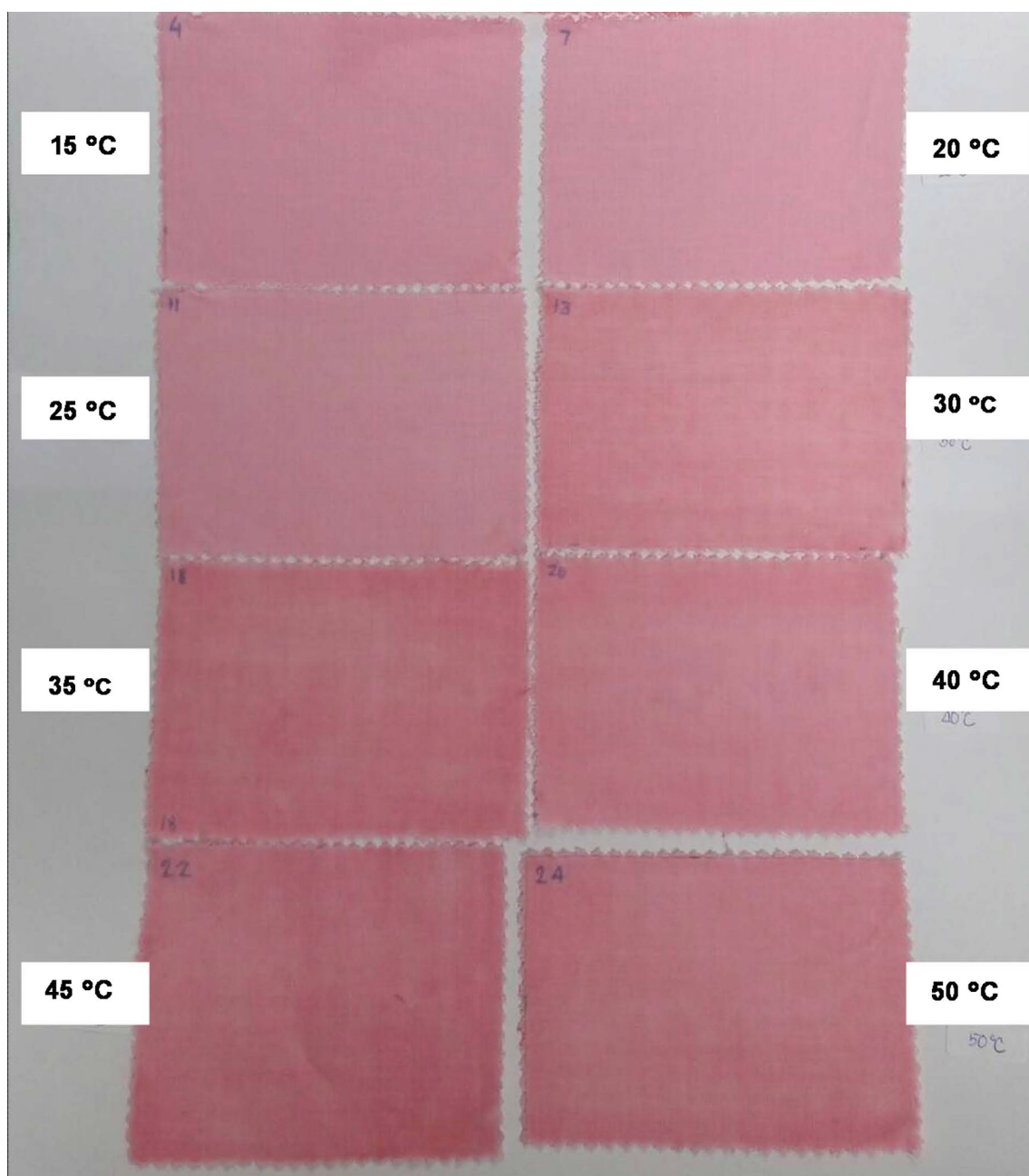


Fig. 6 Picture of washed fabrics at different washing temperatures of 0.3 wt% $C_{12,13}$ -4PO-SO₃Na with 1 wt% NaCl

Table 2 The effect of soiling procedure on detergency performance for polyester

Washing temperature (°C)	Oil removal (%)	
	Not heated soiling (25°)	Heated soiling (40°)
15	63.3 ± 4.12	30.96 ± 2.84
20	73.79 ± 3.69	35.23 ± 1.91
25	75.50 ± 2.80	30.05 ± 3.88
30	31.63 ± 1.84	40.90 ± 3.91
35	35.32 ± 1.24	50.95 ± 1.73
40	36.40 ± 3.02	46.74 ± 2.08

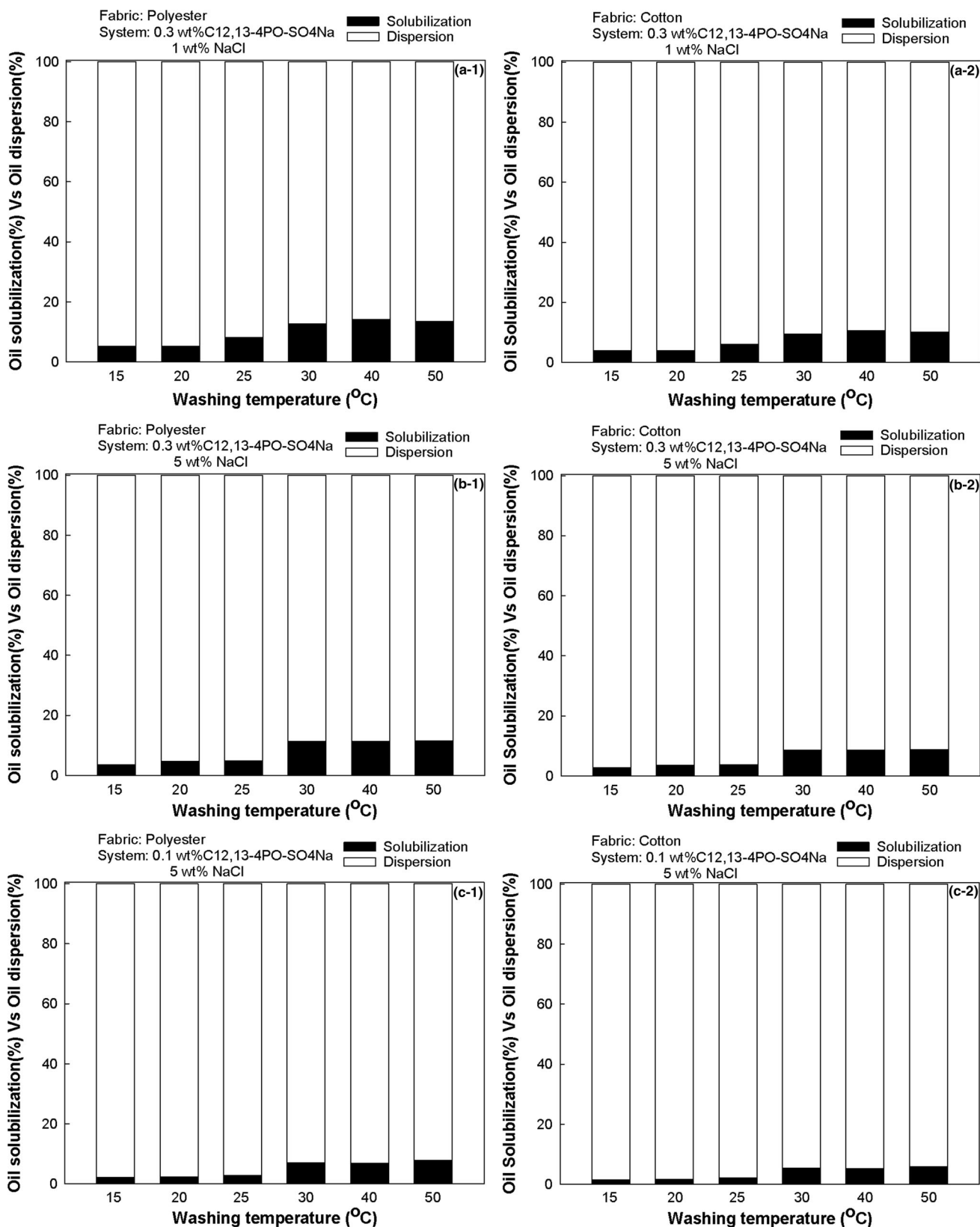
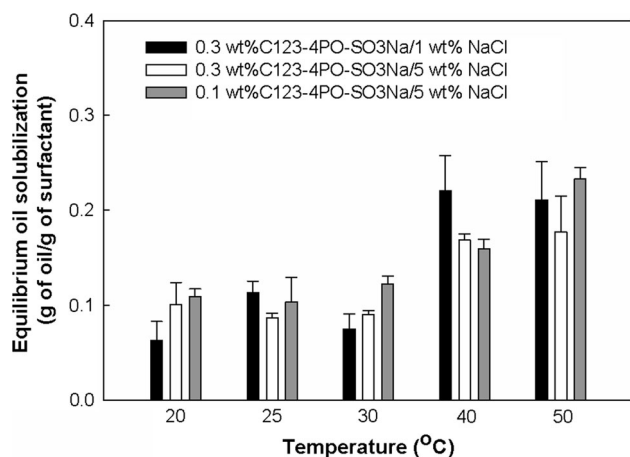


Fig. 7 Solubilized portions and unsolubilized portions of removed oil at 20 min; **a** 0.3 wt% C_{12,13}(PO)₄SO₄Na with 1 wt% NaCl, **b** 0.3 wt% C_{12,13}(PO)₄SO₄Na with 5 wt% NaCl, and **c** 0.1 wt% C_{12,13}(PO)₄SO₄Na with 5 wt% NaCl on both test fabrics of cotton and polyester

Table 3 The ratio of oil solubilization at 20 min to equilibrium oil solubilization with different surfactant systems

Temperature (°C)	Oil solubilization (g/L)		Ratio (At 20 min/at equilibrium)
	At 20 min	At equilibrium	
0.3 wt% C _{12,13} -4PO-SO ₄ Na/1 wt% NaCl			
20	0.0235 ± 0.0035	0.190 ± 0.020	0.1236
25	0.0365 ± 0.0034	0.342 ± 0.012	0.1069
30	0.0570 ± 0.0014	0.226 ± 0.016	0.2519
40	0.0635 ± 0.0233	0.662 ± 0.030	0.0959
50	0.0605 ± 0.0149	0.634 ± 0.033	0.0955
0.3 wt% C _{12,13} -4PO-SO ₄ Na/5 wt% NaCl			
20	0.0210 ± 0.0014	0.304 ± 0.023	0.0691
25	0.0220 ± 0.0056	0.262 ± 0.005	0.0841
30	0.0510 ± 0.0010	0.272 ± 0.004	0.1872
40	0.0520 ± 0.0014	0.506 ± 0.006	0.1028
50	0.0500 ± 0.0028	0.532 ± 0.038	0.0940
0.1 wt% C _{12,13} -4PO-SO ₄ Na/5 wt% NaCl			
20	0.0105 ± 0.0021	0.109 ± 0.008	0.0959
25	0.0125 ± 0.0035	0.104 ± 0.026	0.1202
30	0.0318 ± 0.0017	0.123 ± 0.008	0.2585
40	0.0312 ± 0.0024	0.160 ± 0.009	0.1950
50	0.0350 ± 0.0036	0.233 ± 0.012	0.1502

**Fig. 8** Equilibrium oil solubilization in different surfactant systems as a function of temperature

were a 0.3 wt% surfactant concentration with a 1 wt% NaCl concentration whereas the same surfactant concentration of 0.3 and 5 wt% NaCl were found to be better for a washing temperature above the melting point. Generally, it is known that an increase in temperature results in increasing hydrophilicity of anionic surfactants but non-ionic surfactants have the opposite trend. The studied extended surfactant has the polypropylene oxide groups inserted between the hydrophobic tail and hydrophilic head group, making it less sensitive to temperature than conventional anionic surfactants [39]. This may suggest that the studied extended surfactant has mixed properties

between anionic and nonionic surfactants, explaining good oily detergency over a wide range of washing temperatures.

Figure 5c-2 shows the oil redeposition as a function of washing temperature for both DI water solution and 0.3 wt% surfactant with 1 wt% NaCl concentrations for both polyester and cotton fabrics. For DI water, the oil redeposition reached the maximum at about the melting point for both studied fabrics. For the surfactant solution, the oil redeposition on the cotton fabric reached a slight minimum at the melting point whereas the oil redeposition on the polyester fabric showed a sharp decrease with increasing temperature at the melting point, similar to the decrease in oil removal at the melting point. For cotton, this anomalous behavior is not seen. As shown in Fig. 5a-2, b-2, 0.3 wt% surfactant with 1 wt% NaCl concentration and 0.1 wt% surfactant and 5 wt% NaCl concentration, the oil redeposition generally decreased with increasing temperature just as oil removal generally increased with temperature. So the surprising temperature inversion observed at the melting point, observed only for polyester, is evidenced in both oil removal and oil redeposition.

Solubilization Results

Figure 7 shows both solubilized and unsolubilized portions of removed oil in different washing solutions at different washing temperatures for both test fabrics at 20 min. For any washing temperature, most of removed oil was found to be in a separate dispersed phase (either emulsified liquid

droplets or dispersed solid particles) with a very small portion solubilizing in micelles. The solubilized portion slightly increased with increasing washing temperature. An increase in surfactant concentration from 0.1 to 0.3 wt% increased the solubilization portion of removed oil. This is because an increase in surfactant concentration simply increases the concentration of micelles, leading to an increase in oil solubilization. The results of most removed oil being in free oil particles suggest that the dispersion stability of detached oil particles plays an important role in the overall detergency performance. The differences between the oil solubilization at 20 min and the equilibrium oil solubilization at different temperatures are shown in Table 3. For all studied systems, equilibrium oil solubilization was attained at a very long time (about 24 h). Most of the oil solubilization values at 20 min were around 10% of the equilibrium oil solubilization values, suggesting that the washing time used in the washing experiment as well as in actual application is too short for effective solubilization so most detached oil is in unsolubilized form. Comparing the three surfactant systems in term of g of oil/g of surfactant in Fig. 8 shows that at any temperature below the melting point (~ 30 °C) for all studied surfactant systems, the equilibrium oil solubilization values were almost unchanged with temperature and significantly lower than those at any temperature higher than the melting point. With increasing washing temperature above the melting point, the equilibrium oil solubilization value considerably increased and tended to level off at a temperature around 40–50 °C.

Particle Size Distribution of Detached Oil Particles after Wash Step

Table 4 shows the particle size distribution of methyl palmitate particles suspended in the washing solution after the 20 min wash step for both fabrics using either surfactant or DI water at 25 °C. At 25 °C, the solid nature of the particles of methyl palmitate made it possible to measure the particle size distribution. For any wash system, the particle size distribution of the methyl palmitate solid particles detached from any fabric consisted of a trimodal distribution or three ranges of particle sizes (1–5, 5–100, 100–600 μm). Compared to the surfactant formulation, when DI water was used in the wash step, the detached particles of methyl palmitate had larger sizes in the ranges of 5–100 and 100–600 μm with mean sizes of about 100 and 120 μm for the cotton and polyester fabrics, respectively. Interestingly, the use of surfactant resulted in particle sizes of the detached methyl palmitate solid particles being about one third to one fourth of those of the DI water system. The results suggest that surfactant solution penetrates the methyl palmitate by wetting, the soil is then

Table 4 Particle size distribution and averaged sizes of methyl palmitate after washing step with DI water and surfactant solution with various salinities at 25 °C

Washing solution	Cotton			Polyester			Mean size (μm)							
	1–5 μm	5–100 μm	100–600 μm	1–5 μm	5–100 μm	100–600 μm								
	Size (μm)	Vol. (%)	Size (μm)	Vol. (%)	Size (μm)	Vol. (%)								
De-ionized water	2.32 \pm 0.02	9.45	23.2 \pm 1.11	58.4	282 \pm 5.28	32.2	101 \pm 3.88	2.76 \pm 0.48	6.50	30.0 \pm 0.11	57.1	280 \pm 26.8	36.4	120 \pm 17.8
C _{12,13} (PO) ₄ SO ₄ Na	2.46 \pm 0.01	31	10.6 \pm 0.13	60.8	309 \pm 1.84	8.19	36.2 \pm 1.78	2.51 \pm 0.01	24.1	11.8 \pm 0.06	64.1	313 \pm 12.2	11.7	45.8 \pm 1.41
C _{12,13} (PO) ₄ SO ₄ Na/ 1wt %NaCl	2.39 \pm 0.05	21.5	15.6 \pm 0.51	70.5	276 \pm 9.31	8.02	29.4 \pm 2.47	2.37 \pm 0.01	28.1	13.3 \pm 0.35	62.1	313 \pm 8.07	9.79	40.0 \pm 0.55
C _{12,13} (PO) ₄ SO ₄ Na/ 3wt %NaCl	2.43 \pm 0.11	21.3	14.3 \pm 0.77	74.2	223 \pm 3.48	4.48	21.0 \pm 0.67	2.39 \pm 0.01	26.4	13.1 \pm 0.17	63.6	344 \pm 4.67	10.0	44.4 \pm 1.73
C _{12,13} (PO) ₄ SO ₄ Na/ 5wt %NaCl	2.40 \pm 0.04	32.7	12.6 \pm 1.98	61.8	289 \pm 10.2	5.53	24.1 \pm 3.46	2.37 \pm 0.01	23.9	14.3 \pm 0.51	66.7	335 \pm 3.25	8.81	38.7 \pm 1.81
C _{12,13} (PO) ₄ SO ₄ Na/ 7wt %NaCl	2.37 \pm 0.01	34.8	13.6 \pm 0.04	59.9	348 \pm 2.66	5.34	24.7 \pm 2.62	2.38 \pm 0.11	20.2	15.8 \pm 3.51	71.3	289 \pm 25.9	8.50	37.2 \pm 6.68

Table 5 Point of zero charge (PZC) and zeta potential of methyl palmitate, cotton, and polyester in various solutions at 25 °C

Properties	Cotton	Polyester	Methyl palmitate
Point of zero charge (PZC)	2.90 ^a	2.40 ^a	2.20
Zeta potential (mV) in:			
DI water	-20.3 ± 5.0	-50.0 ± 5.0	-46.2 ± 2.7
0.1 wt% C _{12,13} -4PO-SO ₄ Na	-73.5 ± 6.7	-139 ± 7.6	-157 ± 5.5
0.1 wt% C _{12,13} -4PO-SO ₄ Na/1 wt% NaCl	-54.9 ± 3.4	-60.9 ± 7.2	-57.0 ± 4.3
0.1 wt% C _{12,13} -4PO-SO ₄ Na/3 wt% NaCl	-48.0 ± 4.8	-54.4 ± 4.6	-53.7 ± 2.0
0.1 wt% C _{12,13} -4PO-SO ₄ Na/5 wt% NaCl	-33.3 ± 1.0	-33.1 ± 2.8	-34.1 ± 2.3
0.1 wt% C _{12,13} -4PO-SO ₄ Na/7 wt% NaCl	-30.8 ± 2.7	-28.7 ± 2.5	-29.9 ± 1.2

^a Data from previous work [14]

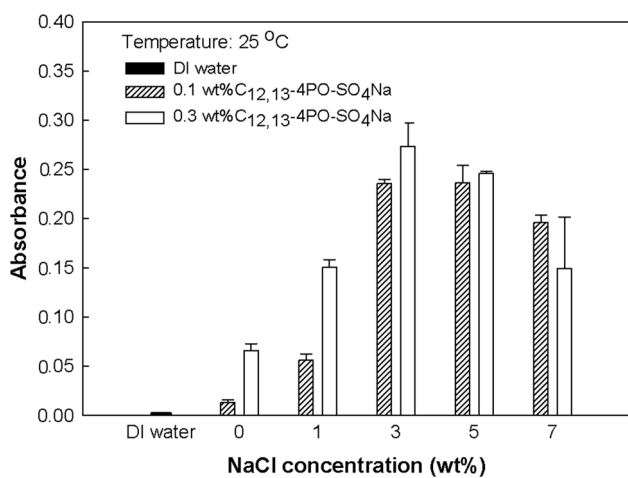


Fig. 9 Dispersion stability (absorbance) of methyl palmitate particles in surfactant solutions as a function of salinity as compared to DI water at 25 °C

dislodged as small particles or droplets, so the small particle size correlates with good wettability leading to high detergency efficiency.

Point of Zero Charge and Zeta Potential Results

Table 5 shows the point of zero charge (PZC) and zeta potential values of methyl palmitate, cotton, and polyester particles in various solution systems at 25 °C (pH 4–6). The PZC values of methyl palmitate, cotton, and polyester were 2.20, 2.90, and 2.40, respectively, indicating that the net surface charges of these three materials are always negative in detergency experiments because of the much higher pH values of both DI water and the studied extended surfactant solutions. The magnitude of the zeta potential of methyl palmitate is high despite it being fairly hydrophobic (contact angle with water of 82°) because of the ester functional group in methyl palmitate which is hydrolyzed into carboxyl and hydroxyl groups to provide negative charges [14, 15, 40, 41]. When DI water was replaced by the 0.1 wt% surfactant solution, the zeta potential of

methyl palmitate became more negative from -46.2 to -157 mV because of the anionic surfactant adsorption. The zeta potential values of both cotton, and polyester in the studied extended surfactant solution became more negative as compared to those in DI water and they also increased when the surfactant concentration increased [42]. This is probably due to higher surfactant adsorption on the solid with higher surfactant concentration, although higher adsorption doesn't necessarily occur since concentrations are well above the CMC. In contrast, with increasing NaCl concentration for any fixed extended surfactant concentration, the zeta potential of methyl palmitate, cotton, and polyester became less negative, due to compression of the double layer or reduction of Debye length next to the surface with increasing ionic strength [43, 44]. A high absolute zeta potential indicates that electrostatic repulsion could be an important factor in dispersion stability [45, 46].

Dispersion Stability

Figure 9 shows the dispersion stability (absorbance) of methyl palmitate solid particles (in terms of average absorbance values) as a function of salinity in the two surfactant systems (0.1 and 0.3 wt%) at 25 °C. The higher the absorbance, the greater the concentration of particles dispersed in the aqueous phase and thus the higher the dispersion stability. The presence of extended surfactant without added NaCl only marginally improved the dispersion stability of methyl palmitate solid particles as compared to DI water despite the fact that the zeta potential is much more negative in the presence of surfactant. Increasing NaCl concentration can greatly improve the dispersion stability; the maximum dispersion stability was found in the salinity range of 3–5 wt% which also produced the best detergency performance. So, dispersion stability is an important component of detergency since the dominant mechanism of solid removal is as particles, not through solubilization. However, the zeta potential decreases in magnitude with increasing NaCl concentration. Comparing effects of surfactant and NaCl

concentrations on zeta potentials and dispersion stability lead to the important conclusion that electrostatic stabilization of the dispersed particles is not the dominant factor in dispersion stability. Dispersion stability is not highest when the zeta potential is at maximum value. Parfitt and Wharton [47] studied the dispersion of solid particles in a surfactant solution and found that the dispersion followed a three-stage process. First, the wettability of solid particle surface occurred, as reflected by the corresponding contact angle. The surfactant solution is better able to penetrate into inter-particle clusters and crevices due to the reduction of the contact angle. Second, the solid particles are suspended in the solution by wetting, and thus dispersion stability occurs. Therefore, deaggregation of the solid

particle is required to achieve a good dispersion by repulsive force between charged particles. After the solid particles have been dispersed in the solution, the danger is that they will coagulate (aggregate) and redeposit. Therefore, the wettability (contact angle), particle size distribution, and dispersion stability of the particles are important to detergency efficiency.

Visual Observations

Figure 10 shows pictures of the washing solutions after the wash step using DI water (Fig. 10a) and two surfactant solutions (0.1 wt% surfactant with 5 wt% NaCl and 0.3 wt% surfactant with 1 wt% NaCl) at temperatures

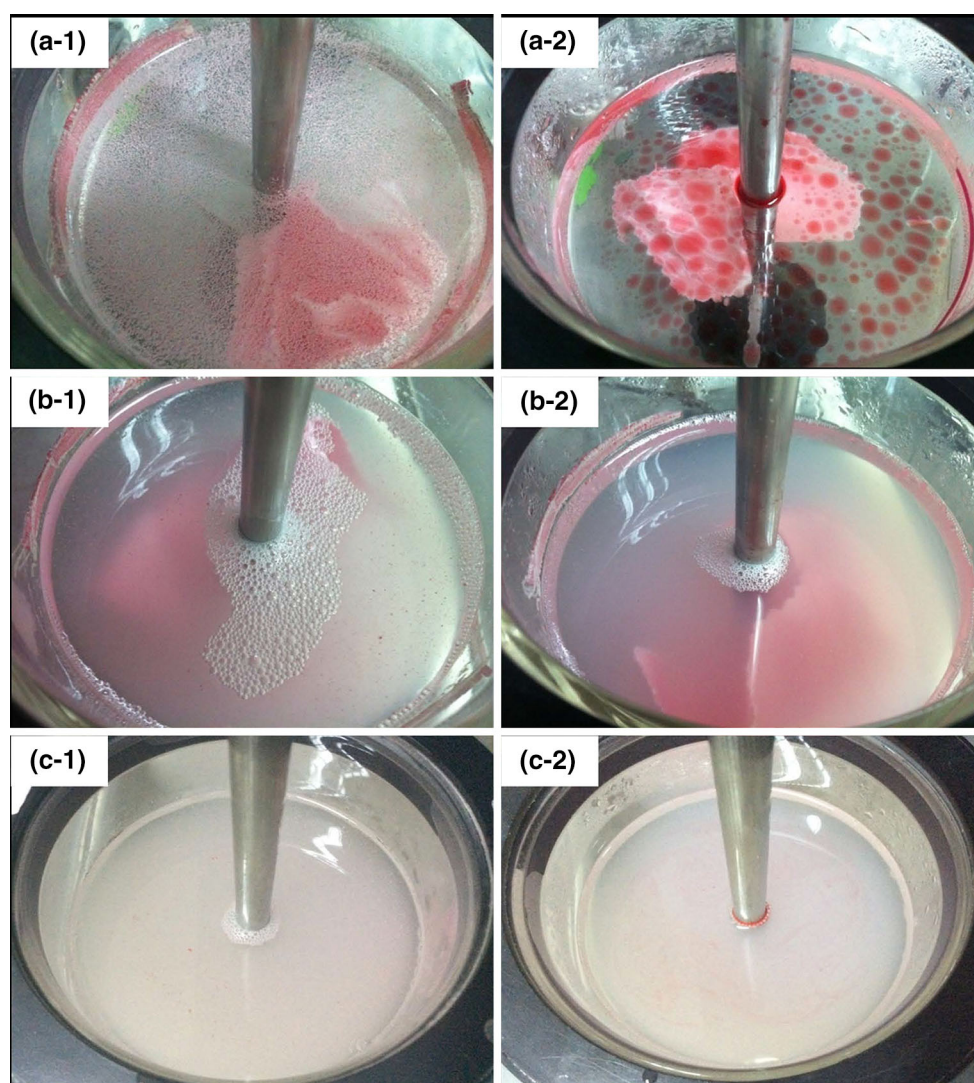


Fig. 10 Photographs of washing solutions after the wash step: **a-1** at below the melting point (25 °C) in DI water, **a-2** above the melting point (35 °C) in DI water, **b-1** below the melting point (25 °C) in 0.1 wt% $C_{12,13}(PO)_4SO_4Na$ and 5 wt% NaCl, **b-2** above the melting

point (35 °C) in 0.1 wt% $C_{12,13}(PO)_4SO_4Na$ and 5 wt% NaCl, **c-1** below the melting point (25 °C) in 0.3 wt% $C_{12,13}(PO)_4SO_4Na$ and 1 wt% NaCl, **c-2** above the melting point (35 °C) in 0.3 wt% $C_{12,13}(PO)_4SO_4Na$ and 1 wt% NaCl

below and above the oil's melting point. In DI water, the removed oil was found mostly in solid particles floating on the surface of the washing solution with relatively large particle sizes at 25 °C and much larger liquid droplets at 35 °C. For detergency with surfactant solutions, the removed oil was found to suspend in the washing solution with much smaller particles and without either solid or liquid methyl palmitate particles or droplets floating on the surface.

Mechanistic Insights

Results on this paper shows the relationships between the removal mechanism of solid fat soil below and above the soil melting point. Above the melting point, lower IFT results in better detergency with varying temperature or salinity. Therefore, roll-up of liquid soil is an important mechanism [6–13]. Below the melting point, the detachment of soil as solid particles occurs by surfactant penetration, leading to the soil breaking up and floating away from the fabric surface into solution as small particles [48–50]. Surfactant and salinity improves wetting, dispersion stability, and decreases detached particle size. Unlike particulate soil, electrostatics are not the primary driving force for detergency.

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