CHAPTER III

MICROEMULSION FORMATION AND DETERGENCY WITH OILY SOILS: II. DETERGENT FORMULATION AND PERFORMANCE

ABSTRACT: In part I of this series, the mixed surfactant system of sodium dioctyl sulfosuccinate (AOT), alkyl diphenyl oxide disulfonate (ADPODS) and sorbitan monooleate (Span 80) was shown to form type I and type III microemulsions with hexadecane and motor oil. In addition, high solubilization and low interfacial tension were obtained between the oils and surfactant solutions both in the supersolubilization region (Winsor type I system close to type III system) and at optimum conditions in a type III system. In the present study, this mixed surfactant system was applied to remove oily soil from fabric (a polyester/cotton blend), with detergency results correlated to phase behavior. Dynamic interfacial tensions were also measured between the oils and washing solutions. In the supersolubilization and in the middle phase regions (type III) much better detergency performance was found for both hexadecane and motor oil removal than that with a commercial liquid detergent product. In addition, the detergency performance of our studied system at low temperature (25 °C) was close to that obtained at high temperature (55 °C), consistent with the temperature robustness of this system's microemulsion phase behavior.

KEY WORDS: Microemulsion, mixed surfactants, detergency, supersolubilization, and dynamic interfacial tension

INTRODUCTION

Detergency, by definition, is removal of unwanted substances, so-called soils, from a solid surface by contacting with liquid (1). It is a complex process in which soil removal is dependent on several factors, such as the nature and composition of the washing solution, type of soil, hydrodynamic conditions, water hardness, temperature, electrolyte level, as well as nature of solid surface. It involves interactions at the air-water, liquid-liquid and liquid-solid interfaces (2).

Soils can be categorized into oily (liquid) or particulate types, with solid nonparticulate (sebum) as a third possible category. We will only address oily soil here; these may be defined as soils which are liquid–like enough to flow and attain an equilibrium contact angle with the substrate being cleaned.

The removal of oily soils from fabric generally occurs by roll up and snap-off (sometimes called emulsification-solubilization) mechanisms (3,4,5). Both roll-up and snap-off are aided by reducing the interfacial tension between oil (soil) and water (bath). Since the lowest oil/water interfacial tensions and highest oil solubilization correspond to microemulsion formation (6), oily soil detergency is often highly dependent on system composition relative to microemulsion phase space. For example, for nonionic surfactant systems, detergency has been related to the phase inversion temperature (PIT) of the system, where oil-water interfacial tensions are at minimum (5,7,8). An anionic surfactant was also found to provide maximum detergency (D_{max}) for the optimum middle phase system where the minimum interfacial tension (IFT_{min}) occurs (9). However, Thompson (10) argued that D_{max} was not always found at IFT_{min}. His work showed that two peaks of maximal detergency were found at different compositions in the removal of hexadecane and triolien by $C_{12}E_5$. In some cases, the separate microemulsion phase (middle phase microemulsion) was trapped in fiber bundles, inhibiting detergency under conditions of IFT_{min} . In this study, we relate microemulsion formation to laundry detergency and attempt to probe this Thompson effect as one goal. Thus to relate microemulsions to detergency performance, the phase behavior of the system has to be well understood. For nonionic systems, temperature is often used to influence microemulsion phase behavior, whereas for anionic surfactant systems, electrolyte

concentration or salinity is often the independent variable used to alter microemulsion characteristics.

Detergency performance is dependent on parameters such as temperature, washing time, agitation speed, and surfactant concentration. Linfield *et al.* (11) conducted a detergency study using a Terg-O-Tometer and found that an increase in agitation speed, washing time, or detergent concentration, produced better fabric detergency performance; for washing conditions at 48.9°C, 0.2% detergent, and 135 ppm water hardness, the maximum detergency was observed at around 150-170 rpm and around 15-20 min washing cycle. A Terg-O-Tometer is generally used to simulate home washing-machine action in a bench scale unit. It consists of four to six stainless steel buckets mounted in a water bath for temperature control. Each bucket is fitted with an agitator similar to a top-loading home washing-machine. Recently, Germain (12) conducted detergency experiments using a Terg-O-Tometer and concluded that several factors such as agitation speed, temperature and amount of detergent should be taken into consideration in optimizing laundering conditions.

In part I of this series (13) we studied the microemulsion phase behavior for hexadecane and motor oil with ternary mixed surfactant system of sodium dioctyl sulfosuccinate (AOT), alkyl diphenyl disulfonate (ADPODS) and sorbitan Table 1 describes the molecular structure and some monooleate (Span 80). properties of these studied surfactants. In that study, we investigated the effect of surfactant composition, salinity (NaCl concentration), and temperature on the type of microemulsion formed (Winsor type I, II, or III), solubilization parameters (oil uptake into microemulsion phase), and interfacial tensions between phases. Ultralow interfacial tensions (e.g. 0.001-0.01 mN/m) were achieved at optimum conditions for both hexadecane and motor oil. In a type I system, where only two phases are present (microemulsion and excess oil), under a condition known as supersolubilization, quite low interfacial tensions are attainable (~0.01 mN/m), not substantially higher than at optimum conditions for a type III system where three phases are present (middle phase microemulsion, excess water, and excess oil) and where minimum interfacial tensions are observed. Comparison of detergency under supersolubilization and under optimum conditions can permit investigation of the Thompson effect.

The objective of the present study is to correlate laundry detergency of hexadecane and motor oil to microemulsion phase behavior. We also compare performance of our system to a commercial laundry detergent. In part III of this series, the detergency mechanisms of oil removal will be discussed in detail.

EXPERIMENTAL PROCEDURES

Materials. Dowfax 8390 is an alkyl diphenyl oxide disulfonate (ADPODS) commercial grade surfactant supplied by Dow Chemical Co. (Midland, MI, USA). The major component of Dowfax 8390 is C_{16} diphenyl oxide disulfonate. Aerosol OT (AOT, 100% solid), dimethyl chloride (99.9% purity), 2-propanol (99.9% purity) and sodium chloride (99% purity) were purchased from Fisher-Scientific (Fair Lawn, NJ, USA). Span 80 was obtained from ICI Uniquema Co. (Wilmington, DE, USA). The chemical structures of the surfactants are shown in Table 1. Hexadecane (99 % purity) and Oil red O (Solvent Red 27, CI. No. 26125) were purchased from Aldrich (Milwaukee, WI, USA). The commercial motor oil for gasoline engines, type SAE 10W-30 (Castrol GTX) was selected in this study. All chemicals were used as received without any further purification. Fabric for detergency tests, a standard unsoiled polyester/cotton (65/35) blend, was purchased from Test Fabrics Co. (Middlesex, NJ, USA).

Fabric preparation and soiling procedure. Before soiling, the fabric was pre-washed to eliminate residues of mill finishing agents which might influence oil removal results. The pre-washing method followed ASTM standard guide D 4265-98 (14). The oil (hexadecane or motor oil) was dyed by an oil-soluble, Oil-red-O dye using the method proposed by Goel (15), before being applied on the fabric. Approximately 0.1 g of oil-soluble dye having λ_{max} around 520 nm was added to 100 mL of the oil. The colored oil was filtered until clear. The soiling procedure was done by diluting 10 mL of the clear dyed oil with dimethyl chloride to 100 mL. The fabric was folded and put in a glass container, into which the dyed oil solution was poured until the fabric was completely submerged. It was left for 1 min before it was rinsed to remove the adhered solution. The soiled fabric was then unfolded and laid on a flat plate to dry under ventilated hood at room temperature over night. After drying, the fabric was cut with pink edge into 3 x 4 inch swatches in the warp and

weft directions. All soiled swatches were kept in a sealed glass container before use. By this soiling method, the average weight ratio of oil to fabric was approximately 0.12 and 0.18 for hexadecane and motor oil respectively. Since a different aging of the soil on textile has an effect on detergency result (16,17), all swatches were freshly prepared for each batch of laundry experiment.

Laundry procedure. A Terg-O-Tometer (Model 7243 USA Testing Co. Inc. Hoboken, NJ) was employed for washing experiments. The washings were performed with 1,000 mL of washing solution, and a 20 min wash cycle with agitation speed at 110 rpm. A 3 min first rinse and 2 min second rinse were performed with deionized water. The water temperatures during both wash and rinse steps were kept constant at 25 °C. Four swatches were washed in each bucket for one cycle as replicants. The washing solution contained 0.112 wt% active surfactants for all washing experiments unless otherwise designated. The percent active concentration was on the basis of total active surfactant in the washing solution. In order to examine the correlation between phase behavior and detergency performance, salt was added to washing solutions so that the salinity corresponded to the microemulsion composition being simulated.

Detergency measurements. Detergency performance was determined by two parameters; reflectance measurement of pre-wash and post-wash swatches, and measurement of residual oil after extraction. Reflectance measurements of the unsoiled swatches, the pre-wash soiled swatches, and the post-wash soiled swatches were conducted by Ultra Scan Sphere Spectrophotometer (Hunter Lab). The detergency (in %) was calculated by the following equation (18):

Detergency (%) = $[(A-B)/(C_0-B)] \times 100$

where A is the average reflectance of the soiled swatches after washing, B is the average reflectance of the soiled swatches before washing and C_o is the average reflectance of the unsoiled swatches before washing. The residual oil was extracted by submerging a swatch in 2-propanol overnight at room temperature and then the absorbance of the extracted solution was measured at 520 nm by a UV/VIS Spectrophotometer (Hewlett Packard 8452 A). The oil removal (%) was obtained from the values of oil levels on the swatch before and after wash. The validity of this method was justified by Goel (15) who showed that the dye and the oil were

removed by the surfactant solution in the same proportion in which they were loaded on the fabric.

In order to fairly evaluate our microemulsion-based formulations, a commercial product (CP) was used under the same laundering conditions. The CP was a liquid detergent having the trade name 'Tide'. It is a product of Procter & Gamble Co. (purchased in May 2002 at Norman, OK), and is the leading commercial heavy-duty liquid laundry detergent in the US based on market share (cited from the news from the website: <u>www.happi.com</u> – Aug. 2002), justifying its selection on an objective basis for comparison process. The percentage of total active surfactants in the commercial liquid detergent is estimated to be ca. 40% as a typical composition of liquid detergents (19).

Measurement of dynamic interfacial tension. Dynamic IFT was measured by a spinning drop tensiometer (model 500, University of Texas, Austin, TX). The dense phase was the aqueous washing solution at 0.112% of our studied formulation (3% AOT, 2% ADPODS and 2% Span 80) at different salinities and the light phase was the dyed oil. The diameters of the oil drop were measured as a function of time.

RESULTS AND DISCUSSION

Microemulsion phase behavior. For the present study, the formulation selected for detergency experiments consisted of 3% AOT, 2% ADPODS and 2% Span 80. The concentration of each surfactant was based on wt% of the total in the aqueous phase. The phase studies were conducted at a volumetric ratio of water to oil of 1 to 1. The phase volumes for each salinity scan system were measured after the systems reached equilibrium. The plots of the volume fraction versus NaCl concentration of the studied system with hexadecane and motor oil are illustrated in Figures 1a and 1b, respectively. The transitions from microemulsion type I to III and to II systems were observed with hexadecane, while only the transition from type I to type III systems was observed with motor oil. The interfacial tensions at supersolubilization (type I just at the type III boundary) and at the optimum in the middle phase for both hexadecane and motor oil are summarized in Table 2. For the studied systems with a water to oil ratio equal to one, the salinity values were found around 5% and 8% NaCl at the supersolubilization region for hexadecane and motor oil, respectively.

The optimum (where interfacial tension is a minimum and oil and water solubilization into the microemulsion is equal) salinity values were 8% and 16% NaCl for hexadecane and motor oil, respectively.

Dynamic interfacial tension. In detergency experiments, the washing solution to oil ratio was much higher than the 1:1 ratio used in the phase studies. In addition, the washing solution in this study contained only 0.112% active concentration of mixed surfactants. As a result, the equilibrium phase behavior in the washing bath may be different from the results from the phase studies conducted at an oil/water ratio of 1 to 1. Also, since phase behavior equilibrium times can be weeks or months as compared to a 20 min wash cycle, dynamic IFT values may more accurately represent washing conditions if they differ from equilibrium values. Therefore, to obtain a better understanding of the washing process, dynamic IFT values between the washing solution and the dyed oils were determined to more closely simulate the actual situation in the washing bath. The values of dynamic IFT at various salinities of both systems (hexadecane and motor oil) are illustrated in Figures 2 and 3, respectively. As expected, as the salinity in the microemulsion systems approaches the optimum salinity, the interfacial tension between oil and water phases decreases. The dynamic IFT reached equilibrium in a very short period of time both for the hexadecane and the motor oil, except at the highest salinities of 8% and 16%, respectively. The spontaneous reduction of the dynamic IFT within a few minutes may result from microemulsion formation at the interfacial region between the surfactant solution and the stain oil on the fabric during the washing process. Under the studied condition, the IFT values are in the range 0.001 to 0.10 mN/m, which is believed to be excellent for a detergency application.

By comparing the dynamic interfacial tension curves in Figures 2 and 3 for hexadecane and motor oil, respectively to the equilibrium interfacial tension values presented in Table 2, we can conclude that during the washing cycle (20 minutes), the equilibrium interfacial tension of optimum formulation (8% NaCl for hexadecane and 16% NaCl for motor oil) can be achieved. On the other hand, for the supersolubilization case, the interfacial tension obtained after 20 minutes (Figures 2 and 3) are considerable higher than the equilibrium supersolubilization boundaries obtained from the equilibrium phase studies (5% NaCl for hexadecane, and 8% NaCl for motor oil).

This observation suggests that in washing conditions, the supersolubilization might have shifted to higher salinity values. In the subsequent discussion on detergency at supersolubilization for the motor oil case, we will refer as the supersolubilization condition that of 12% NaCl instead of the initial 8% NaCl obtained from equilibrium data. There are two potential reasons that could have been responsible for the shift of the supersolubilization for the system with motor oil; the difference of the oil/water ratio; and the difference of total surfactant concentration in the system. Another potential reason may be considered in the real washing situation at supersolubilization is a slow relaxation kinetics (6) due to the low coalescence rate of a system at supersolubilization. This could make the IFT value between oil and the washing solution in a washing bath is not as low as equilibrium condition. However, the coalescence study is beyond the scope of this present study, it will be recommended for the future study.

Detergency performance: effect of salinity. Based on the results of the phase behavior of our studied formulation (3% AOT, 2% ADPODS and 2% Span80), the microemulsion system exhibited a sensitivity to salinity typical of anionic surfactant systems (13). Thus the present study utilized salinity as the variable parameter to induce different microemulsion types. The detergency results of the studied system at different salinities for hexadecane and motor oil removal are shown in Figures 4a and 4b, respectively. The cleaning performance is presented both in terms of detergency from the change in reflectance and oil removal. Kissa (1) noted that a reflectance change (ΔR) might not be proportional to oil removal; nonetheless, in this study there is a good correlation between these two methods of characterizing detergency. Increasing the salinity up to the optimum system significantly improved the detergency performance for the case of motor oil removal. The result show that our formulation effectively removed hexadecane even at very low salinity, while motor oil required higher salinity. For instance, to reach 70% removal, the salt level was around 0.1 % NaCl for hexadecane removal but as high as 12% NaCl for motor oil removal. This is because the motor oil is more hydrophobic and more complex in composition than hexadecane. Raney (20) showed that a ratio of nonionic/anionic

surfactants ($C_{12}EO_3/C_{12}LAS$) of 76:24 gave the optimum detergency for hexadecane (removal around 63% at 25°C), whereas for the present system at 8% NaCl and 25 °C hexadecane removal was found to be higher than 80%. However, the active concentration of total surfactants in Raney's study was only 0.05 wt%, which is about half of that used in this study.

From the present study, even at the lowest salinity, 0.128% NaCl, the motor oil removal was found to be much higher when compared to a study by Chi and Obendorf (21). They conducted a detergency study on a polyester/cotton blend soiled with used motor oil by using a commercial powder detergent. According to their results, the oil removal was less than 5% under their washing conditions; 12 min wash, 1 min rinse in 100 ppm hardness water, at 34 °C and 44 g per 69 L or around 0.064% detergent concentration. Even though the result may not be directly comparable to our study since the motor oil used may be different in composition and the difference in washing condition, nonetheless the performance of our formulation seems to be very promising.

Correlation of microemulsion formation and detergency performance. Figures 5 and 6 show oil removal and IFT between washing solution and oil as a function of salinity for hexadecane and motor oil, respectively. The oil removal with the same active concentration (0.112%) of CP (no salt) is also illustrated in Figures 5 and 6 for comparison. To relate the phase study with the washing result, for the system of hexadecane, at 5% NaCl was referred as the formulation in supersolubilization region whereas at 8% was a type III system based on dynamic IFT values. Similarly, in the washing solution with motor oil, the systems at 12% and 16% NaCl were in the supersolubilization and middle phase, respectively. As be seen in Figures 5 and 6, the removal of both oils increases slightly when shifting from the supersolubilization region to the middle phase even though the IFT decreases by one or two orders of magnitude from the supersolubilization region to the middle phase or type III system of hexadecane and motor oil, respectively. As expected, the supersolubilization region is reasonably efficient for detergency application since it still offers both high solubilization and relatively low IFT. In addition, the detergency result of our formulation shows better performance

compared to the CP at any salinity above 0.1% NaCl and above 3% NaCl for hexadecane and motor oil removals, respectively.

The results from this present study confirm the correlation of improving detergency with decreasing IFT, consistent with several previous studies (7,8,20,22). However, in these studies supersolubilization has not been mentioned. Only the work by Thompson (10) revealed that the D_{max} did not always correspond to the IFT_{min}. Besides IFT_{min}, contact angle is another parameter influence to D_{max} . Moreover, Thompson's work mentioned that the adhesive and cohesion work between oil and substrate are important mechanisms for oil removal. For our studies, a much more detailed mechanistic interpretation is given in part III of this series.

Temperature effect. Hexadecane detergency was studied at 55°C to compare to the base case of at 25 °C. As shown in Figure 7, the detergency efficiency increases slightly with increasing temperature from 25 to 55 °C for hexadecane with the studied formulation. The microemulsion phase behavior of our system, which was a mixed system of anionic and nonionic surfactants, was fairly insensitive to temperature due to the opposing effect of temperature on anionic and nonionic surfactants that compensated each other. It is known that for an ionic surfactant system, an increase in temperature leads to increasing HLB of the system while for a nonionic surfactant system, the HLB of system decreases as temperature increases. For our formulation, even though the temperature effect on nonionic surfactant (Span 80) compensated that of anionic surfactants (AOT and ADPODS), the higher proportion of the two ionic surfactants still made the mixed formulation slightly influenced in the direction of ionic surfactant system (13).

Solans and Azemar (9) found that the detergency performance tended to be independent of temperature for an anionic surfactant system. Their study showed the maximum detergency for hexadecane removal by using a 1.0 wt% mixture of sodium dodecyl sulfate and n-pentanol with 10% NaCl both at 20°C and 55°C. Besides impacting the HLB of a system, an increasing temperature also influences the physical properties of the system. For example, an increasing temperature is believed to enhance oil mobilization due to reduced oil viscosity (23,24). This may be a reason for the slightly better performance of our formulation at a higher temperature. Nonetheless, it can be concluded that our system is robust with respect to

temperature, as was previously observed in microemulsion phase behavior (13). This mean that a properly designed formulation can work efficiently over a wide range of temperature, an obvious advantage in laundry detergency, particularly in regions where heated water is used in fabric detergency and water temperatures can vary widely.

Detergency performance: compared to commercial product. Figure 8a shows the comparison of the detergency results for hexadecane removal as a function of the total active concentration of our microemulsion-based formulations and the commercial liquid detergent. In this experiment, the washing was conducted using the supersolubilization system (5% NaCl). The total active concentration refers to the wt% of the total surfactants in the solution. The results showed that for any active concentration greater than 0.1%, our formulation gave around 20% higher detergency than that of the commercial liquid detergent (CP). The highest detergency reached was 65% at around 0.25% or higher active concentration of the studied formulation. Solans and Azemar (9) reported that 80% detergency was achieved for a pure nonionic surfactant, C₁₂EO₄ with the same polyester/cotton fabric. However, the active concentration used in their study was 1% which is 4 times higher than that used in the present study. Goel (22) studied detergency as a function of temperature for 1% $C_{12}EO_{14}$. The detergency was presented as the change in reflectance before and after wash (ΔR) at 520 nm, which was 10.6 for the maximum detergency, compared to ca. 14 for hexadecane removal in the current study.

For motor oil, supersolubilization system based on dynamic IFT study (12% NaCl) was also selected for this experiment. It was found that the detergency reaches the plateau at about 0.2% active concentration for our formulation as shown in Figure 8b. For the CP formulation, at the highest active concentration of 0.65% the detergency performance had not yet reached a plateau. Obviously, for any given active concentration, the commercial liquid (CP) gave much lower efficiency in detergency (about 30%) than our formulation. In addition, the percentage of liquid detergent is usually recommended at around 0.6 to 1.2 % in the washing solution or around 0.3 to 0.8% active surfactant if we consider the liquid detergent as a without builder type which contain active surfactant at around 55 wt% (25). In this range of

surfactant concentrations for household application, our formulation showed much better detergency performance than the commercial liquid detergent for removal of both oils from the fabric.

Even though our formulation in the supersolubilization region shows very promising results for both hexadecane and motor oil removal as compared to the CP, we recognize that at the high salinities, 5% NaCl for hexadecane and 12% NaCl for motor oil, may not be practical in a real detergency application. However, from our previous study on phase behavior (13), we found that to maintain the phase behavior of the system, a reduction of salinity can be achieved by an increase in the proportion of lipophilic surfactant (e.g. AOT and Span 80) in the mixed surfactant composition, which should be studied in future research. However, the purpose of this study was to establish the relationship between microemulsion phase behavior and laundry detergency both under conditions of minimum interfacial tension (type III systems) and supersolubilization. These results clearly show that the detergency was outstanding for either choice of microemulsion phase space.

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REFERENCES

- 1. Kissa, E. Evaluation of Detergency, in *Detergency Theory and Technology* edited by W.G. Cutler and E. Kissa, Marcel Dekker, New York, 1987, p. 2
- Rybinski, W. Surface Chemistry in Detergency in Handbook of Applied Surface and Colloid Chemistry, edited by K. Holmberg, D.O. Shah, and J.S. Milan, John Wiley & Sons, Ltd, West Sussex, UK, 2002, Vol. 1, p. 53.
- Dillan, K.W., E.D. Goddard, and D.A. McKenzie, Oily Soil Removal from a Polyester Substrate by Aqueous Nonionic Surfactant Systems, J. Am. Oil Chem. Soc. 56:59 (1979).
- 4. Broze, G., Detergents and Cleaners, in *A Handbook for Formulators*, edited by K.R. Lange., Hanser, Munich, Germany, 1994, p. 29.
- Miller, C.A., and K.H. Raney, Solubilization Emulsification-Mechanisms of Detergency, *Colloids and Surf. A* 74:169 (1993).
- 6. Bourrel, M. and R.S. Schechter, *Microemulsions and Related Systems*, Marcel Dekker, New York, 1998, p.335.
- Mori, F., J.C. Lim, O.G. Raney, C.M. Elsik, and C.A. Miller, Phase Behavior, Dynamic Contacting and Detergency in System Containing Triolien and Nonionic Surfactants, *Colloids Surf.*, A 40:323 (1989).
- Azemar, N., The Role of Microemulsions in Detergency Processes, in Industrial Applications of Microemulsions, edited by C. Solans and H. Kunieda, Marcel Dekker, New York, 1997, p. 375.
- Solans, C. and N. Azemar, Detergency and HLB Temperature in Organized Solutions edited by S.E. Friberg and B. Lindman, Marcel Dekker, New York, 1992, p. 273.
- 10. Thompson, L., The role of Oil Detachment Mechanism in Determining Optimum Detergency Conditions, J. Colloid Interface Sci, 163:61 (1994).
- Linfield, W.M., E. Jungermann, and J.C. Sherrill, Establishment of a Standardized Detergency Evaluation Method, J. Am. Oil Chem. Soc. 39:47 (1962).
- 12. Germain, T., Understanding Terg-O-Tometer Testing Variables, Paper presented on AOCS Annual Meeting, Montreal, Canada, 5-8 May, 2002.

- Tongcumpou, C., E.J. Acosta, L.B. Quencer, A.F. Joseph, J.F. Scamehorn, D.A. Sabatini S. Chavadej and N. Yanumet, Using Surfactant Mixture Formation and Detergency with Oily Soils: I Phase Behavior and Interfacial Tension, submitted to J. Surfact. Deterg.
- ASTM D 4265-98 Standard Guide for Evaluating Stain Removal Performance in home Laundering, *Annual Book of ASTM Standards*, Vol. 15.04, American Society for Test and Materials, West Conshohocken, PA. 2000.
- Goel, S.K., Measuring Detergency of Oily Soils in the Vicinity of Phase Inversion Temperatures of Commercial Nonionic Surfactant Using an Oil-Soluble Dye, J. Surfact. Deterg. 1:221 (1998).
- Chi Y.S., and S.K. Obendorf, Aging of Oily Soils on Textiles: Chemical Changes upon Oxidation and Interaction with Textile Fibers, J. Surfact. Deterg. 1:371 (1998).
- Chi Y.S. and S.K. Obendorf, Aging of Oily Soils on Textiles Material: A literature Review, J. Surfact. Deterg. 1:407 (1998).
- ASTM D 3050-98 Measuring Soil Removal from Artificially Soiled Fabrics, *Annual Book of ASTM Standards*, Vol. 15.04, American Society for Test and Materials, West Conshohocken, PA. 2000.
- Christ, T., W.W. Morgenthaler, and F. Pacholec, Laundry products in Detergents and Cleaners A Handbook for Formulators, edited by K.R. Lange, Hanser Publishers, Cincinnati, 1994, p.133.
- Raney, K.H., Optimization of Nonionic/Anionic Surfactant Blends for Enhanced Oily Soil Removal, J. Am. Oil Chem. Soc. 68:522 (1991).
- Chi, Y.S., and S.K. Obendorf, Detergency of Used Motor Oil from Cotton and Polyester Fabrics, J. Surfact. Deterg. 2:1 (1999).
- Goel, S.K., Phase Behavior and Detergency Study of Lauryl Alcohol Ethoxylates with High Ethylene Oxide Content, J. Surfact. Deterg. 3:221 (2000).
- 23. Powe, W.C., Removal of Fatty Soils from Cotton in Aqueous Detergent Systems, J. Am. Oil Chem. Soc. 40:290 (1963).
- 24. Kissa, E., Kinetics of Oily Soil Release, Text. Res. J. 41:760 (1971).

- 25. Jakobi, G., and A. Löhr, *Detergents and Textile Washing*, Henkel, Düsseldorf, Germany, 1987, p. 107.
- 26. Wu, B., Formulation of petroleum microemulsions systems for surfactantenhanced in-situ subsurface remediation, M.S. Thesis, University of Oklahoma, 1996, p. 15
- Kunieda, H., Formation of Liquid Crystals in Dilute Mixed Surfactants Systems in *Mixed Surfactant Systems*, edited by K. Ogino, and M. Abe, Marcel Dekker, New York, 1992, p. 235.

Table 1

Properties of Surfactants Used in the Study

Chemical Name	Chemical Formula/Structure	MW	HLB
Alkyl diphenyl oxide disulfonate, ADPODS (Dowfax 8390)	SO ₃ ⁻ Na ⁺ SO ₃ ⁻ Na ⁺	642	> 40*
Bis (2-ethylhexyl) sulfosuccinic acid sodium salt (AOT) (dioctyl sulfosuccinate)	O O SO 3'Na ⁺	444	10.2**
Sorbitan monooleate (Span 80)		428.6	4.3

- Note * For Dowfax 8390, the HLB is not available, however, it is reported that its HLB is higher than sodium dodecyl benzene sulfonate whose HLB is around 40 (26)
 - ** HLB value in a 1% brine (27)

Table 2

Salinity and IFT in the Supersolubilization Region and at Optimum Conditions for the System of 3% AOT, 2% ADPODS, and 2% Span 80 (Initial aqueous solution to oil volume ratio equals 1:1 at equilibrium)

Oil	Salinity for	Salinity at	IFT wm/O	IFT* at
	SPS	Optimum, S*	for SPS	Optimum, S*
	(% NaCl)	(% NaCl)	(mN/m)	(mN/m)
Hexadecane	5.0	8.0	0.0093	0.0042
Motor oil	8.0	16.0	0.0221	0.0142

Note SPS is supersolubilization



FIG. 1 Phase diagrams of the system of 3% AOT, 2% ADPODS and 2% Span 80 with salinity scan for (a) hexadecane and (b) motor oil; initial volume ratio oil to water = 1:1, and S* is optimum salinity. Dashed line corresponds to the type I/III and type III/II boundary and the type I/III boundary corresponds to supersolubilization.



FIG. 2 Dynamic IFT of hexadecane and washing solution containing 0.112 % active concentration of surfactants at different salinities



FIG. 3 Dynamic IFT of motor oil and washing solution containing 0.112 % active concentration of surfactants at different salinities



FIG. 4 Detergency performance for hexadecane and motor oil removal for our formulation (3% AOT, 2% ADPODS and 2% Span 80) at 25 °C, 0.112% active surfactant concentration and various salt concentrations comparing with D.I. water and commercial liquid detergent (CP); where SPS is our formulation in the supersolubilization region and S* is the optimum salinity at equilibrium from phase studies.



FIG. 5 Hexadecane removal with the studied formulation compared to the commercial liquid detergent (CP) and the interfacial tension between the oil and washing solution at various salt concentrations; where SPS is our formulation in the supersolubilization region and S* is the optimum salinity at equilibrium from phase studies.



FIG. 6 Motor oil removal with our formulation compared to the commercial liquid detergent (CP) and the interfacial tension between the oil and washing solution at various salt concentrations where SPS is our formulation in the supersolubilization region and S* is the optimum salinity at equilibrium from phase studies.



FIG. 7 Detergency performance for hexadecane removal at two different temperatures for our formulation



FIG. 8 Comparison of detergency performance of our microemulsion-based formulation of 3% AOT, 2% ADPODS, and 2% Span 80 at supersolubilization (5% and 12% NaCl with hexadecane and motor oil, respectively) with commercial liquid detergent (CP) at different active concentrations.