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Increasing the Solubility Enhancement of Anionic DOWFAX Surfactants

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ABSTRACT

Previous research has demonstrated the robust nature of DOWFAX surfactants for enhanced subsurface remediation. However, these surfactants are not as effective as others in enhancing contaminant solubility. A series of experiments evaluated various methods of increasing the solubility enhancement of the DOWFAX components (i.e., using a cosurfactant, adding an electrolyte, and forming middle-phase microemulsions). Results demonstrate that while increasing the alkyl chain produced slight increases in contaminant solubility, middle-phase microemulsions produced the greatest enhancements. Middle-phase microemulsions were produced using an electrolyte, isobutanol, a cosurfactant, and one of the DOWFAX components. Middle-phase microemulsions increased contaminant solubilities by one to two orders of magnitude over DOWFAX surfactants alone, and by three to four orders of magnitude relative to water. Thus, DOWFAX-based microemulsion systems have the potential to significantly enhance contaminant solubility and expedite environmental remediation.

INTRODUCTION

Contaminated aquifers have traditionally been remediated by flushing the formation with water, followed by treatment and reinjection of the extracted

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water (pump-and-treat). However, this approach has proven ineffective, frequently due to the presence of trapped oil phases (1). As a result, surfactant-enhanced subsurface remediation is being considered as a method of enhancing pump-and-treat remediation.

Previous research has shown that surfactants can enhance the "aqueous solubility" and thus the removal efficiency of various organic contaminants as compared to water alone. In one study, six nonionic and four anionic surfactants were evaluated for enhancing the removal of automatic transmission fluid from sandy material (2). Results showed an increase from 23% removal by water alone to averages of 68 and 70% removal by ionic and nonionic surfactants, respectively. Anionic surfactants have also been evaluated for increasing the solubility of phenanthrene (3). At concentrations between 10 and 30 mM, which is above the critical micelle concentration (CMC), virtually all the phenanthrene was recovered in the aqueous phase. In another study an anionic surfactant enhanced the solubility of naphthalene by 30 times that of water alone (4).

Surfactant-enhanced remediation research initially focused on the solubilization mechanism [i.e., surfactant micelles enhance contaminant solubility by partitioning of the contaminant into the hydrophobic micelle interior (5–7)]. For a given surfactant and contaminant, the solubility enhancement can be quantified by the micelle–water partition coefficient (K_m), which is the ratio of micellar to aqueous contaminant concentrations (based on molar ratios X_m and X_a, respectively):

$$K_m = X_m/X_a$$

K_m is thus analogous to Henry's constant which describes the partitioning of a contaminant between gaseous and aqueous phases. For a given surfactant, K_m values increase with increasing contaminant hydrophobicity.

Recent research has shown that middle-phase microemulsions (Winsor Type III systems) can enhance removal efficiencies by one to two orders of magnitude beyond solubilization (Winsor Type I systems) while using the same surfactant concentration (7, 8). A Winsor Type III system occurs when the surfactant system is at the incipient point of leaving the water phase and going into the oil phase (or vice versa). At this incipient point all the surfactant wants to accumulate at the interface, but since it can not, a new surfactant-rich middle phase occurs. This middle-phase microemulsion produces ultrahigh contaminant solubility and ultralow interfacial tensions between the water and oil phases (9, 10).

The hydrophilic–lipophilic balance (HLB) is one measure of a surfactant systems' preference for the water or oil phase. High HLB systems are very hydrophilic and will prefer the water phase while low HLB systems are more lipophilic (hydrophobic) and will prefer the oil phase. Adjusting the HLB of the surfactant system can thus make it water or oil-soluble, or under select conditions can produce a middle-phase microemulsion. Depending on the surfactant(s), different methods can be used to alter the system HLB. For a given class of surfactants, increasing the alkyl chain length will decrease the surfactant HLB, while for anionic surfactants, electrolyte addition will decrease the system HLB. Mixing two surfactants with differing HLB values will produce a mixed system with an intermediate HLB value. Adding a hydrophobic alcohol (e.g., butanol or pentanol) can also alter the system HLB and help form a middle-phase microemulsion. These methods of altering the system HLB and forming middle-phase microemulsions have been evaluated for a variety of surfactants and contaminants (8–10).

Implementing surfactant-enhanced remediation depends ultimately on economic feasibility. Minimizing surfactant losses is critical to the implementation of this technology (11). Previous laboratory and field studies have demonstrated that DOWFAX surfactants are very resistant to sorption and precipitation losses (12, 13). These desirable characteristies are somewhat offset by the greater solubility enhancement of other surfactants, with middle-phase microemulsions demonstrating the highest solubility enhancement (to our knowledge, middle-phase microemulsions have not been reported for DOWFAX surfactants and environmental contaminants). This research thus seeks to improve the solubility enhancement of DOWFAX surfactants. The overall hypothesis of this research is that the solubility enhancement of DOWFAX surfactants will improve as the system moves from a Winsor Type I system toward a Type III system, and that maximum enhancement will occur within a Winsor Type III system (middle-phase microemulsion). We will use the general approaches described above for altering the HLB of surfactant systems and approach and/or produce middle-phase microemulsions.

Specific objectives of this research were as follows: 1) to evaluate the solubility enhancement of DOWFAX components with increasing hydrocarbon chains, 2) to investigate the use of a mixed-surfactant (anionic/nonionic) system to enhance contaminant solubility (using DOWFAX surfactants along with a low HLB nonionic surfactant), and 3) to evaluate the solubility enhancement of the DOWFAX components while approaching and within middle-phase microemulsion systems (by adding alcohols and electrolytes to the system evaluated in Objective 2). While this research focuses on one specific group of anionic surfactants, the general approach used is applicable to other anionic surfactant systems.

MATERIALS AND METHODS

The contaminants evaluated in this study are phenanthrene (Acros Organics, New Jersey, 98+% purity) and tetrachloroethylene (PCE, Aldrich Co., Chemical Properties of Contaminants (16, 17)

Contaminant	Formula	Molecular weight (g/mol)	Density (g/cm^3)	Aqueous solubility (mg/L)	Log K_{OW}[a]
Phenanthrene	$C_{14}H_{10}$	178.2	1.18	1.00	4.52
Tetrachloroethylene (PCE)	C_2Cl_4	165.8	1.62	150	2.60
Sodium chloride	NaCl	58.4	2.17	3.6×10^5	NA[b]
Isobutanol	$C_4H_{10}O$	74	0.81	7.4×10^4	NA[b]

[a] K_{OW} = octanol–water partition coefficient.
[b] NA = not applicable.

Milwaukee, WI, 99%). Sodium chloride and isobutanol (Fisher Scientific) were used in middle-phase microemulsion studies. Table 1 gives properties of the chemicals used in this study. All chemicals were used as received.

The ionic surfactants used in this study were components of the DOWFAX series obtained from the Dow Chemical Co. (Midland, MI). The DOWFAX surfactants are alkylated diphenyloxide disulfonates and can be mono- or dialkylated and mono- or disulfonated. The nonionic surfactants used were from the Igepal series and were either octyl- or nonylphenyl ethoxylates [with six to eight ethylene oxide (EO) groups], as obtained from Rhone-Poulenc (Cranbury, NJ). All surfactants were used as received. Tables 2 and 3 list properties of the DOWFAX and Igepal surfactants, respectively.

Batch studies were conducted in 40 mL EPA vials with Teflon-lined screw caps. Experiments were conducted at room temperature (~23–24°C). All

TABLE 2
Fundamental Properties of DOWFAX Components

Surfactant[a]	Average molecular weight	CMC (mM)[b]
C10 MAMS	422	0.38
C10 MADS	523	0.14
C12 MAMS	451	NA[c]
C12 MADS	550	0.13
C16 MADS	600	0.25
C20-24 MADS	656	NA[c]

[a] C## = alkyl chain length; M = mono; D = di; A = alkyl; S = sulfonate.
[b] Provided by Dow Chemical Co.
[c] NA = not available.

TABLE 3
Fundamental Properties of Igepal Surfactants[a]

Surfactant[b]	Molecular weight	Density	HLB[c]	Cloud point (°C)	Moles of EO[d]
CA-620	514	1.05	12	21-24	7-8
CO-610	570	1.05	12.2	22-28	7.7
CO-530	484	1.04	10.8	50-60	6

[a] Information provided by Rhone-Poulenc Surfactant & Specialties.
[b] CA = octylphenylethoxylate; CO = nonylphenylethoxylate.
[c] HLB = hydrophilic–lipophilic balance.
[d] EO = ethylene oxide.

batch systems contained an excess contaminant phase, which was visually verified at equilibrium. The vials were agitated on a wrist action shaker for 24 hours and then allowed to equilibrate for at least another 24 hours prior to analysis. All samples were injected through a 0.2-μm filter prior to HPLC analysis. To evaluate the solubility enhancement of increasing carbon chain length surfactants, 35 mL of each component (C10 to C20–24 MADS) were added to 0.2 g phenanthrene and shaken for 24 hours. Surfactant concentrations were varied from 0 to 100 mM and the resulting contaminant concentrations were measured. The slope of the resulting plot is the molar solubilization ratio (MSR = moles of contaminant solubilized per mole of surfactant in micelles). From the MSR, one can calculate the micelle water partition coefficient (K_m) as follows:

$$K_m = [C_0/S]\,[\mathrm{MSR}/(1 + \mathrm{MSR})]$$

where C_0 is the molar concentration of water and S is the molar solubility of the contaminant (6, 8).

Cosurfactant experiments were conducted to determine the Igepal surfactant which produced the greatest solubility enhancement of the C16 MADS. This was done by adding each nonionic surfactant to C16 MADS, along with 0.2 g of phenanthrene (which is equivalent to 32 mM—phenanthrene water solubility is 5.6×10^{-3} mM), with subsequent shaking for 24 hours. After selecting the nonionic cosurfactant (CO-530), batch studies were conducted using Igepal CO-530 and various C16 MADS concentrations to determine the optimum surfactant ratio. The optimum ratio was then used to determine the K_m value for the cosurfactant system for comparison with the C16 MADS-only K_m value.

Middle-phase microemulsions studies were carried out in Kimble 15 mL graduated test tubes using DOWFAX and Igepal surfactants along with isobutanol and electrolytes (sodium or calcium chloride). The solutions were shaken by hand for approximately 1 minute and allowed to settle. Using a 1:1 oil-to-water ratio, 5 mL of various surfactant solution was added to 5 mL of PCE. NaCl and isobutanol were added to the system at various concentrations until a middle phase was visually observed. The total weight-based percentages of NaCl and isobutanol necessary to form a middle phase were then determined. Select systems were reproduced on a larger scale (in a separatory funnel) to allow quantitative HPLC analysis of the middle-phase system. The same technique was used with $CaCl_2$ instead of NaCl to compare the use of a monovalent versus divalent electrolyte.

HPLC analyses for phenanthrene and PCE were conducted using a UV wavelength of 260 and 254 nm, respectively. A flow rate of 1.0 mL/min was selected, and 80% methanol (Fisher Scientific Co., HPLC grade) was used as the mobile phase. All HPLC analyses were performed on a Beckman System Gold Liquid Chromatograph (Beckman Instruments, Inc., San Ramon, CA) with a 150 × 4.6 mm Nucleosil C18 reverse-phase column (Alltech Associates, Inc., Deerfield, IL).

RESULTS AND DISCUSSION

The first objective of this work was to compare the solubility enhancement of varying alkyl length components of the DOWFAX series. Figure 1 shows phenanthrene solubility as a function of increasing DOWFAX component concentrations. By comparing all four components at a given surfactant concentration (e.g., 38 mM), the phenanthrene concentration (solubility) is seen to be 0.25, 0.80, 2.17, and 2.42 mM for C10, C12, C16, and C20–24, respectively. It is observed that for a given surfactant concentration, the phenanthrene solubility increases as the surfactant chain length increases. Thus longer alkyl chain DOWFAX surfactants do increase the solubility enhancement of contaminants, as long as the surfactant maintains its water solubility and does not phase separate (which ultimately limits the effectiveness of this approach).

The slope of the plots in Fig. 1 is the molar solubilization ratio (MSR) which can be used to calculate the micelle–water partition coefficient (K_m), as discussed above. From Fig. 1 it is observed that as the carbon chain length increases, the degree of solubility enhancement also increases (i.e., the slope of the line increases). This is shown as well in Table 4, which demonstrates that the MSR and K_m values increase with increasing chain length (statistically significant with 95% confidence). The C20–24 MADS results are not summarized in Table 4 due to the nonlinear nature of these data. As seen in Fig. 1, the C20–24 data are higher than the C16 data at lower surfactant concentrations but lower than the C16 data at higher surfactant concentrations. While we can speculate that the C20–24 DOWFAX surfactant exceeded its solubility

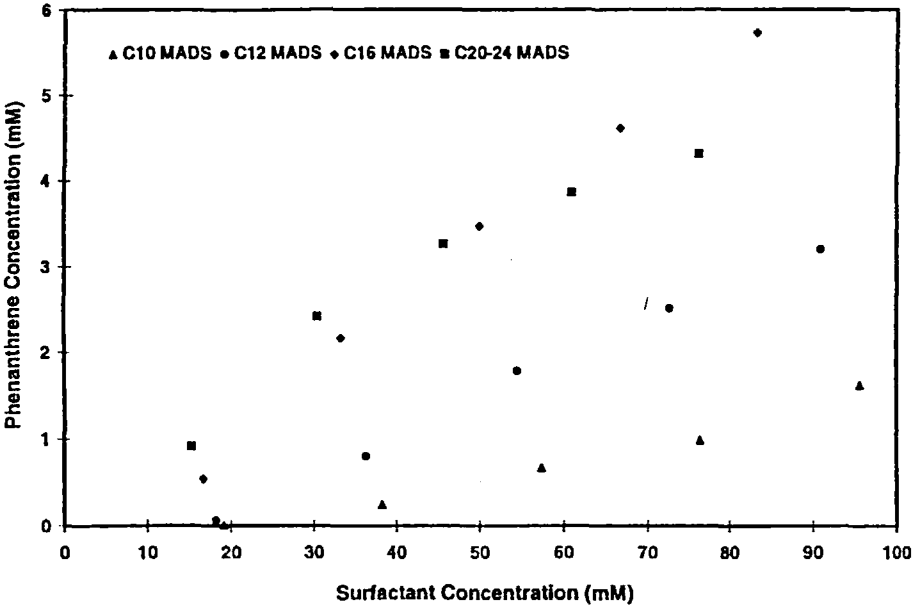

FIG. 1 Enhanced phenanthrene solubility for various DOWFAX components as a function of surfactant concentration.

at higher concentrations, no visual evidence of this was observed. Future research should further explore this phenomenon. Solubilization studies were also conducted with PCE in C10 MADS and C16 MADS. The resulting MSR values were 0.539 and 1.153, respectively, and the corresponding log K_m values were 4.60 and 4.79, respectively.

The second objective of this research was to determine if a mixed surfactant system would increase the solubility enhancement of phenanthrene in C16

TABLE 4
Phenanthrene Molar Solubility Ratio (MSR) and Micelle-Water Partitioning Coefficients (K_m) for DOWFAX Surfactants (see Fig. 1)

Surfactant	C10 MADS	C12 MADS	C16 MADS
MSR	0.023 ± 0.006[a]	0.044 ± 0.006	0.077 ± 0.014
Log K_m	5.35 ± 0.09	5.62 ± 0.06	5.85 ± 0.07

[a] 95% confidence interval.

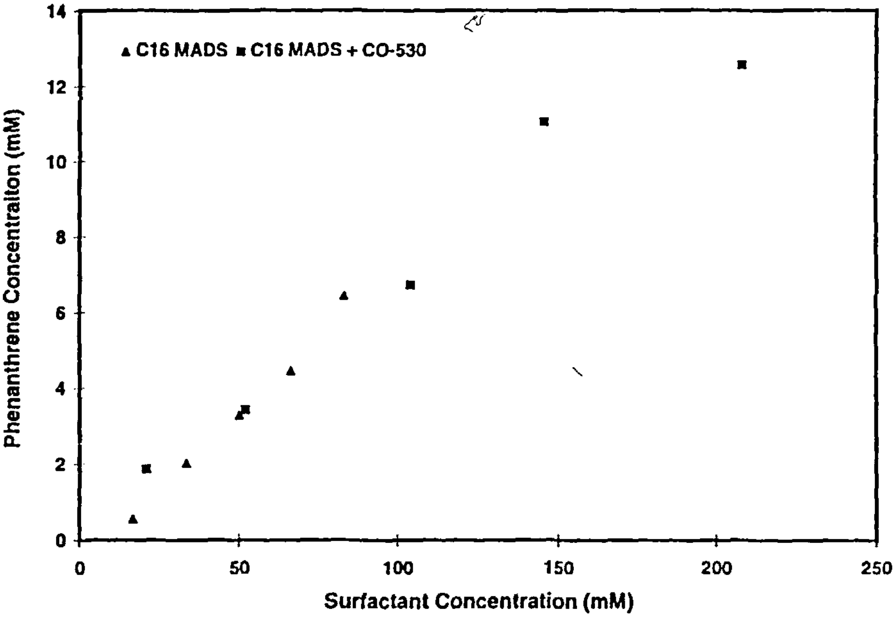

FIG. 2 Enhanced phenanthrene solubility with and without CO-530 as cosurfactant (5/1 ratio of *C16 MADS to CO-530).*

MADS. Figure 2 illustrates the use of a cosurfactant system (a weight ratio of 5/1 with C16 MADS and CO-530 was used). The CO-530 was chosen based on its low hydrophilic–lipophilic balance (HLB). It was hypothesized that in addition to the mixed micelle effect, the low HLB CO-530 would move the mixture closer to a Winsor Type III system and thus further improve the solubility enhancement. By comparing the two systems in Fig. 2 at 20 mM C16 MADS, the C16 MADS alone solubilizes 0.56 mM phenanthrene while the use of a cosurfactant increases phenanthrene solubility to 1.87 mM. Therefore, at low concentrations there is a definite increase in phenanthrene solubility for the mixed micelle. This is likely due to the micelle being a predominantly nonionic surfactant at lower surfactant concentrations. Nonionic surfactants typically have higher K_m values than anionic surfactants: Table 5 shows that CO-530 alone does have a higher K_m value than C16 MADS (statistically significant at the 95% confidence interval). However, the data in Table 5 demonstrate that the K_m value for the mixed CO-530–C16 MADS system is not statistically different from the C16 MADS system alone. This demonstrates that mixed micelles alone will not produce significant

TABLE 5
Phenanthrene Molar Solubility Ratio (MSR) and Micelle-Water Partitioning Coefficients (K_m) for C16-MADS and/or CO-530 (from Fig. 2)

Surfactant	C16 MADS	CO-530	C16 MADS + CO-530
MSR	0.077 ± 0.014[a]	0.131 ± 0.02	0.061 ± 0.02
Log K_m	5.85 ± 0.07	6.06 ± 0.07	5.76 ± 0.12

[a] 95% confidence interval.

solubility enhancements over the anionic surfactant system. These results are consistent with previous findings (14).

The third objective of this study was to evaluate the formation and efficiency of middle-phase (Winsor Type III) systems for enhancing contaminant solubility. While guided by the HLB concept (i.e., the nonionic surfactant and alcohol were chosen based on HLB considerations as discussed above), producing a middle-phase microemulsion remains a trial-and-error process. The first middle-phase system was realized in a solution of 50 mM C16 MADS and 10 mM CO-530 along with isobutanol and either sodium or calcium chloride. Figure 3 is a phase boundary diagram for this system with

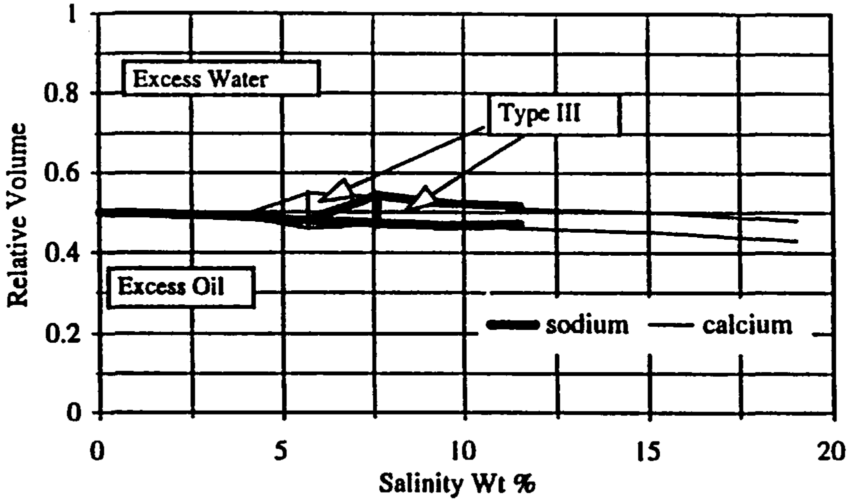

FIG. 3 Middle phase microemulsion phase diagram for 50 mM C16 MADS and 10 mM CO-530 with varying sodium or calcium aqueous concentration and 3.82 wt% isobutanol. The volumetric ratio of PCE to water is 1.0 (5 mL of each). The vertical lines in the Type III region correspond to middle phase microemulsion with the maximum volume.

TABLE 6
PCE Solubility in 50 mM C16 MADS + 10 mM CO-530 Alone and with Other Variables Which Together Produce a Middle-Phase Microemulsion (data correspond to maximum middle-phase systems in Fig. 3)

Solution[a]	mM PCE[c]
50:10 C16 MADS/CO-530	7.8
50:10 Surfactant + 7.63% NaCl	24.9
50:10 Surfactant + 3.82% isobutanol	9.3
50:10 Surfactant + 7.63% NaCl + 3.82% isobutanol[b]	201

[a] Percentages are weight based on total system.
[b] Middle phase.
[c] PCE water solubility = 0.9 mM. PCE solubility in 50:10 surfactant + 5.7% $CaCl_2$ + 3.82% isobutanol = 320 mM.

increasing NaCl and $CaCl_2$ concentrations. When no sodium or calcium is added (the left side of the figure), we have equal volumes of water and PCE. Increasing electrolyte concentrations decreased the HLB of the surfactant system and was able to produce a middle-phase microemulsion system. For example, at 5.7 wt% $CaCl_2$ the middle-phase volume is maximized and we have 4.7 mL of PCE, 4.4 mL of water, and 0.9 mL of middle-phase microemulsion. For NaCl the middle-phase volume was maximum at 7.6 wt%—as expected, using $CaCl_2$ reduces the amount of electrolyte necessary to produce a middle phase.

Table 6 shows the measured PCE concentration for the middle-phase microemulsion with the maximum volume (PCE concentration of 201 mM for 7.6 wt% NaCl). This value is over 200 times greater than the PCE water solubility of 0.9 mM. Table 6 also shows the PCE solubility in individual components of the middle-phase system (i.e., the two surfactants without alcohol or NaCl, and the alcohol or NaCl alone). While the PCE concentrations of these systems are an order of magnitude higher than water solubility, they are an order of magnitude lower than when combined to form a middle-phase microemulsion. This emphasizes the increased solubility enhancement of the middle-phase microemulsion versus the individual components. These results are especially encouraging as a previous study demonstrated that C16 DOWFAX surfactants and salinity alone could not produce a middle-phase microemulsion (15).

The data in Fig. 4 show the impacts of increasing the surfactant concentrations on the middle-phase systems. By comparing Figs. 3 and 4 it is observed that the volume of the middle-phase microemulsion increases as the surfactant concentration increases and that the middle phase first appears at lower NaCl

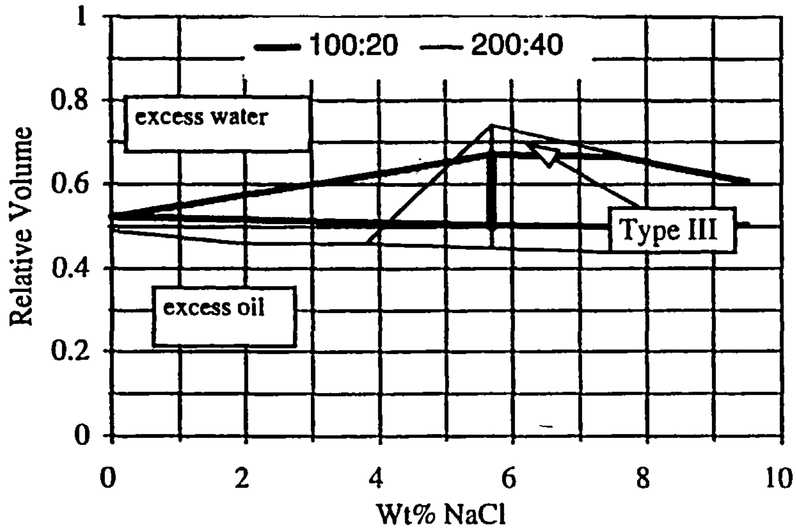

FIG. 4 Impacts of increasing surfactant concentration on the middle phase microemulsion for aqueous salinity scan (100 mM C16 MADS + 20 mM CO-530 versus 200 mM C16 MADS + 40 mM CO-530). Isobutanol is 7.63 wt%. The volumetric ratio of PCE to water is 1 (5 mL of each). The vertical lines in the Type III region correspond to middle phase microemulsion with the maximum volume.

levels for the higher surfactant concentration. The data in Table 7 show that for the higher surfactant concentration the PCE solubility increased (497 versus 201 mM) and the NaCl level decreased for the middle-phase system with the maximum volume (7.6 versus 5.7 wt%).

TABLE 7

PCE Solubility in Higher Surfactant Concentration System (100 mM C16 MADS + 20 mM CO-530) with Other Variables Which Together Produce a Middle-Phase (data correspond to maximum middle-phase system for 100:20 system in Fig. 4)

Solution[a]	mM PCE
100:20	24
100:20 + 5.73% NaCl	45
100:20 + 7.63% isobutanol	43
100:20 + 5.73% NaCl + 7.63% isobutanol[b]	479

[a] Percentages are weight based on total system.

[b] Middle phase.

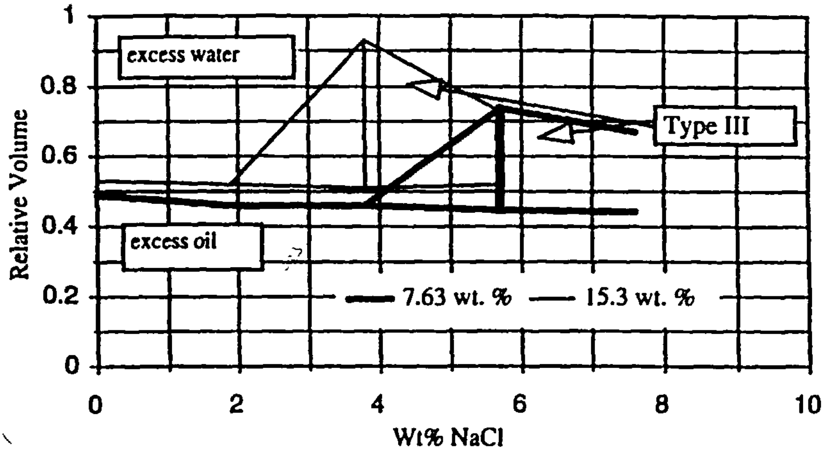

FIG. 5 Impacts of increasing isobutanol concentration on the middle phase microemulsion for 200 mM C16 MADS + 40 mM CO-530 with salinity scan. The volumetric ratio of PCE to water is 1 (5 mL of each). The vertical lines in the Type III region correspond to middle phase microemulsion with the maximum volume.

Figure 5 shows the results of increasing the isobutanol concentration from 7.63 to 15.3 wt% for a surfactant solution of 200 mM C16 MADS + 40 mM CO-530. The data in Figure 5 show that doubling the concentration of isobutanol decreases the weight percent of NaCl required to form a middle phase while increasing the volume of middle phase present. While the volume of the middle phase increases, Table 8 documents that the PCE concentration decreases from 572 mM PCE to 371 mM PCE (i.e., more of the middle phase is made up of water, as visually observed in Fig. 5).

TABLE 8

PCE Solubility in Highest Surfactant Concentration System (200 mM C16 MADS + 40 mM CO-530) at Two Isobutanol Concentrations (from Fig. 5) and for $CaCl_2$ (data not shown)

Solution[a]	mM PCE
200:40 + 7.63% isobutanol + 5.7% NaCl[b]	572
200:40 + 15.3% isobutanol + 3.8% NaCl[b]	371
200:40 + 15.3% isobutanol + 2.2% $CaCl_2$[b]	416

[a] Percentages are weight based on total system.

[b] Middle phase.

It should be noted that laboratory studies are conducted under highly controlled conditions. Inherent heterogeneities in field parameters (e.g., contaminant distribution) can impact the performance of middle-phase microemulsions identified in laboratory studies. For example, the oil-to-water ratio in the field is variable and at times different from that studied in the laboratory. This variation can impact the performance of middle-phase systems—i.e., changing water-to-oil ratios encountered in the field will alter system performance (18). At the same time, recent laboratory (19) and field (20) studies have demonstrated that even if the optimum middle-phase system is not achieved under field conditions, the performance of this somewhat less than optimal system is still much greater than surfactant-enhanced solubilization alone. This is especially encouraging as it demonstrates that middle-phase systems are more robust than they may initially appear.

CONCLUSIONS

Based on results of this research, the following conclusions are suggested.

1. Increasing the surfactant alkyl chain length produced minor increases in the solubility enhancement.
2. The use of a nonionic cosurfactant did not significantly increase the solubility enhancement of the C16 MADS surfactant.
3. Middle-phase microemulsions greatly increased the solubility enhancement of the DOWFAX components, and the solubility enhancements were significantly greater than for the surfactants, electrolyte, or isobutanol alone.

We have demonstrated that middle phase systems can significantly increase solubility enhancement of the DOWFAX surfactants. This higher efficiency along with the robust nature of DOWFAX surfactants further increases their usefulness for environmental remediation. At the same time, while this research has focused on one specific class of anionic surfactants, the approach described can be applied to other systems as well.

GLOSSARY

CMC	critical micelle concentration
C_0	molar concentration of water
DADS	dialkylated disulfonate
DAMS	dialkylated monosulfonate
HLB	hydrophilic–lipophilic balance
K_m	micelle water partition coefficient
MADS	monoalkylated disulfonate

MAMS	monoalkylated monosulfonate
MSR	molar solubilization ratio
PCE	perchloroethylene (tetrachloroethylene)
S	contaminant water solubility (molar basis)
X_a	contaminant mole ratio in aqueous phase
X_m	contaminant mole ratio in micelle phase

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