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PHASE-BEHAVIOR-BASED SURFACTANT–CONTAMINANT SEPARATION OF MIDDLE PHASE MICROEMULSIONS

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ABSTRACT

This research studied separation of contaminants solubilized in middle phase microemulsions by shifting the contaminant-rich microemulsions from Winsor type III to type I systems. Precipitation-based exchange of polyvalent cations (Al^{3+} and Ca^{2+}) with equivalent amounts of a monovalent cation (Na^+) broke the middle phase microemulsions. Most of the contaminants solubilized in the middle phase microemulsion separated as free phase contaminant due to the much lower solubilization capacity of the resulting type I system. The phase transitions between Winsor type III and type I systems were reversible with the precipitation and re-dissolution of the polyvalent cations, allowing subsequent reuse of the surfactant solution. The phase transitions brought about by deprotonation/protonation of oleic acid, an organic additive used to

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promote formation of middle phase microemulsions, were also studied. The neutral form of oleic acid was more effective than its dissociated anion for promoting the formation of middle phase microemulsions, but oleic acid in the middle phase microemulsions could not be deprotonated by adding aqueous OH^-. On the other hand, the oleate anion could be protonated even when it was in middle phase microemulsions because of its relative distribution in the systems. While exchange of surfactant counterions could separate contaminant solubilized in middle phase microemulsions, transformation of oleic acid in middle phase microemulsion systems did not produce the desired result.

INTRODUCTION

Surfactant-enhanced aquifer remediation (SEAR) is an excellent alternative to the traditional pump-and-treat technology for remediation of subsurface non-aqueous phase liquid (NAPL) contamination. Surfactants can greatly increase the solubilization of organic contaminants and reduce the interfacial tension (IFT) between contaminants and the aqueous phase, thereby substantially accelerating the remediation processes. Surfactant systems can be designed to reduce the IFT between the NAPL and water by several orders of magnitude, thereby overcoming the capillary forces trapping the residual NAPL and releasing the contaminant as both middle-phase microemulsion (in which NAPL is solubilized) and free phase (enhanced mobilization mechanism). Surfactant solutions can also increase the apparent solubility of the NAPL by several orders of magnitude via micellar solubilization, removing the residual NAPL by dissolution (enhanced solubilization mechanism). Generally, the solubilization mechanism is preferred for dense NAPLs in an effort to minimize downward migration potential (1), while the recovery by mobilization and solubilization into a middle-phase microemulsion is most efficient for light NAPLs (2). Although surfactant solutions with electrolyte concentrations close to their optimal salinities can easily achieve ultra-low IFTs (generally less than 10^{-3} dynes/cm) to mobilize NAPLs from subsurface, contaminant separation and surfactant reuse are still desirable for such remediation schemes because of the surfactant cost and waste stream disposal.

BACKGROUND

Surfactants are amphiphilic, surface-active molecules, consisting of both hydrophilic and hydrophobic groups. Above a certain concentration, known as

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the critical micelle concentration (CMC), surfactant molecules aggregate together to form micelles. In the micelles, surfactant molecules are oriented such that their hydrophilic head groups shield the hydrophobic tail groups from the water environment. Contaminant partitioning into the resulting hydrophobic micellar core increases the contaminant's apparent solubility. Due to the size and structural limitation of the micellar core, a maximum solubilization capacity exists. Middle phase (Winsor type III) microemulsions have a bi-continuous structure (3,4), which is composed of alternate layers of contaminant and water with surfactant molecules partitioning in between. In an optimal system, up to 50% (vol.) of the middle phase microemulsion is composed of the contaminant.

Middle phase microemulsions are much more efficient at solubilizing contaminant than Winsor type I microemulsions. Contaminant solubilization in Winsor type I systems is dependent on many factors, including electrolyte concentration, surfactant concentration, temperature, presence of hydrotropes, etc. If a Winsor type III microemulsion is converted to a type I, the surfactant molecules will migrate into the aqueous phase in the form of micelles, which have a lower solubilization capacity towards the contaminant. This will result in the release of a large portion of the contaminant solubilized in the middle phase as free phase contaminant. The lower the contaminant solubilization capacity of the resulting micelles, the greater the fraction of the contaminant that will be released as free phase. Therefore, middle phase microemulsions can be decontaminated if the phase behavior is shifted from a Winsor type III to a type I. Microemulsion phase transitions can be promoted by adjusting the hydrophilic interactions, lipophilic interactions, simultaneous interactions, and entropic effects in the surfactant system (5). In this research, cation exchange (which altered the system's hydrophilic interactions) and organic additive transformation (which altered the system's lipophilic interactions) were studied to promote phase transitions.

The HLB (hydrophilic–lipophilic balance) of a surfactant system is a parameter that characterizes a surfactant's tendency to reside in the water or oil phase, or form a middle phase microemulsion. Transition of microemulsion systems from Winsor type III to type I can be accomplished by increasing the surfactant system HLB through adjusting relevant parameters. Similarly, by decreasing the surfactant solution HLB, the middle phase microemulsion will reappear. While an ionic surfactant is assigned a single HLB value, electrolytes or organic additives can adjust the effective HLB value of its solution to produce an optimal middle phase microemulsion with a contaminant. A salinity scan, typically used to achieve this goal, is a systematic HLB scan by varying the electrolyte concentration. With a given contaminant, the HLB of the surfactant system will be reduced and the microemulsion phase will transition in the order of Winsor type I-type III-type II microemulsions as the salinity increases (6–8). Fig. 1 shows the typical phase transitions of contaminants with increasing EACN (equivalent alkyl carbon number) values using salinity scans. Contaminants with high EACNs require surfactant systems with lower HLB values (i.e., high electrolyte concentrations) to form optimal microemulsions.

Besides adding electrolytes, organic additives (e.g., alcohols and hydrotropes) can also help to optimize microemulsion formation through lipophilic interactions. Alcohols play a two-fold role in microemulsion formulation: adjusting the surfactant partitioning between aqueous and oil phases (as co-solvent), and stabilizing the microemulsion by preventing the formation of rigid phases (as co-surfactant) (9). Organic hydrotropes can enhance the interactions between contaminant and surfactant molecules, and promote formation of a middle phase microemulsion. They also bring other benefits to the microemulsion systems, and short chain carboxylic acids have been applied in this manner (9). Recently, incorporation of hydrophilic/lipophilic linkers in surfactant system formulation has been proposed to reduce the surfactant concentration necessary to achieve desired microemulsion phase behavior (10,11). A hydrophilic linker promotes the interactions of surfactant head groups with water molecules, while a lipophilic linker enhances the interactions of surfactant tail groups with the organic molecules. Oleic acid (*cis*-9-octadecenoic

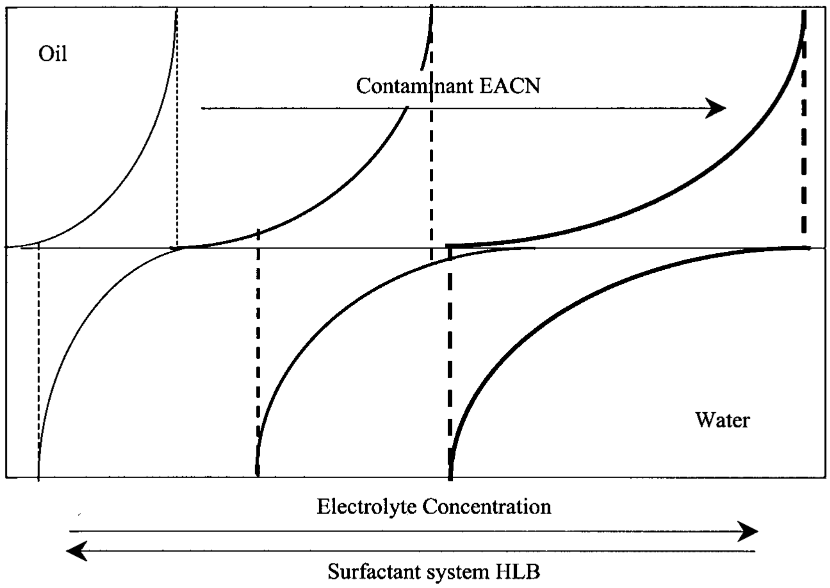

Figure 1. Effect of electrolyte additions on microemulsion phase behavior between an ideal ionic surfactant solution and contaminants with increasing EACN values.

acid) had been found to be a very good lipophilic linker in surfactant systems to promote middle phase microemulsion formation (10). If the organic additive in the microemulsion system is removed or transformed to another form that has much less interactions with the system, a shift from Winsor type III microemulsion to type I in phase behavior is expected.

Removal of polyvalent cations from solutions can be accomplished through precipitation, according to the solubility products of the species. Polyvalent cations associate more strongly to the micelles of anionic surfactant than monovalent cations, which leads to easier formation of Winsor type III and II systems (5). Calcium salt has been successfully applied in surfactant formulations in both laboratory (12) and field studies (13,14) for NAPL remediation. Aluminum salt can also be potentially used in surfactant system formulation for SEAR, although there are some application concerns (15). Polyvalent cations, such as Al^{3+} and Ca^{2+}, have much higher surface charge densities than a monovalent cation like Na^+. They are thus much more effective at 'salting out' surfactant molecules and decreasing the system HLB to promote formation of middle phase microemulsion. Therefore, even though the equivalent surfactant counterion concentration (in eq/L) remains the same after polyvalent cations have been precipitated as hydroxide or carbonate, a shift in the microemulsion phase behavior towards Winsor type I will occur after such cation exchange.

Most of the contaminant solubilized in a middle phase microemulsion will be released as free phase contaminant when the system transitions from a Winsor type III to a type I. After separating the organic phase and the precipitate, the aqueous phase can be reused, with the addition of polyvalent cation supplement. However, the presence of the monovalent cations added for precipitation purposes will reduce the amount of the polyvalent cations required to re-form a Winsor type III system with the contaminant. Micellar-enhanced ultra-filtration (MEUF) can be coupled with the cation precipitation/supplement processes to concentrate surfactant micelles while allowing the separation of excess electrolyte from the surfactant solution (16,17).

Although organic molecules are difficult to selectively remove from solution, those with basic or acidic functional groups (e.g., $-NH_3$, $-COOH$) can be transformed by reaction with H^+ or OH^- in solution. Compared to exchanging the surfactant counterions in microemulsion systems through cation precipitation, the adjustment of solution pH is much more convenient. Unlike most hydrotropes (e.g., alcohols), long chain organic acids can be deprotonated/protonated through reaction with strong bases/acids. In the case of oleic acid, the non-dissociated molecules are neutral and hydrophobic, while their anionic form has both hydrophobic and hydrophilic moieties. The lipophilic interactions in the surfactant system will be altered with deprotonation/protonation of such organic additives, resulting in corresponding phase transitions.

OBJECTIVES AND HYPOTHESES

The primary objective of this research was to study the separation of contaminants solubilized in middle phase microemulsions by shifting the microemulsion from a Winsor type III to a type I. This research also sought to evaluate the roles of cations with different charge valency and organic acids in different forms (protonated vs. deprotonated) in microemulsion phase behavior. Both exchanging the surfactant counterions through precipitation and transformation of the functional group of organic additive molecules were evaluated as methods of achieving the phase transition. It was hypothesized that with appropriate surfactant system selection, a Winsor type III microemulsion could be shifted back to a type I by replacing the polyvalent cations with equivalent amounts of monovalent cations brought about by cation precipitation. It was also hypothesized that pH adjustment could deprotonate/protonate oleic acid molecules in microemulsion systems and cause desired microemulsion phase transition.

MATERIALS AND METHODS

Properties of the surfactants and contaminants studied in this research are summarized in Tables 1 and 2, respectively. Aluminum salt ($AlCl_3$), calcium salt ($CaCl_2$), and sodium salt (NaCl) were selected as the electrolytes (in the order of decreasing cation surface charge density). Isopropanol (IPA) was used as a co-solvent in some surfactant system formulations. A.C.S. reagent grade $CaCl_2$, NaCl, NaOH, Na_2CO_3, HCl, IPA, trichloroethylene (TCE), and 98% $AlCl_3$, 90% oleic acid, 99+% decane, and 99+% tetradecane were purchased from Aldrich (Milwaukee, WI) and used as received. Sodium oleate solutions were prepared from the reaction of stoichiometric amounts of oleic acid and NaOH. The pH of surfactant solutions after acid or base additions was measured with pH paper with accuracy of ± 0.5 pH unit, which adequately indicated the significant pH changes in this research (between 2 and 10).

Salinity scans were conducted by adding 5.0 mL of organic liquids into 15 mL vials along with 5.0 mL of solutions containing surfactant and electrolyte/organic additive. The vials were then completely mixed and allowed to equilibrate for 48 hr for complete phase separation. All experiments were conducted at a room temperature of 23 ± 1°C. The phase volumes of different phases were recorded and normalized for comparison. Under-optimal middle phase microemulsion systems (having electrolyte concentrations just inside the Winsor type III region) instead of optimal systems were evaluated to balance the desired IFT reduction with the chemical consumption necessary to shift the microemulsion phase behavior. Concentrated strong acid and base solutions were

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Table 1. Fundamental Properties of Surfactants

Surfactant	Ave. M.W.	Designed Molecular Formula	CMC (mg/)L	Active (%)	Supplier
Aerosol MA	376	$C_6H_{13}OOCH_2CH(SO_3Na)COOC_6H_{13}$	5,200[a]	80	CYTEC Industries, Inc. (Willow Island, WV)
Alfoterra 145-4PO sulfate	559	$C_{14.5}H_{30}(C_3H_7O)_4SO_4Na$	250[b]	30.8	Condea Vista Company (Austin, TX)

[a] From Ref. (3).
[b] Measured by authors.

used to alter the pH of solutions to minimize volume changes. Precipitation of Al^{3+} was achieved by adding 12 *M* NaOH solution into vials containing the microemulsions and the changes in the phase behavior were recorded after equilibrating for 4 hr. 8 *M* HCl was then added to dissolve the precipitated Al^{3+} and the change in phase behavior was recorded again after 4 hr. Ca^{2+} precipitation was achieved by adding 2 *M* Na_2CO_3 solution to the vial containing the microemulsion system, and re-dissolution of precipitated Ca^{2+} was achieved by adding 8 *M* HCl solution. Transformation of organic additives was conducted in a similar way: 12 *M* NaOH was used to deprotonate oleic acid while 8 *M* HCl was used to protonate the oleate anions. Total volume changes brought about by addition of reagents were negligible. A centrifuge was used when necessary to accelerate phase separations. Surfactant concentrations are given in M (mol/L) in the results and discussions, while the corresponding weight percentage concentrations (%) are also given in parentheses the first time they appear.

RESULTS AND DISCUSSIONS

Cation Exchange—Al^{3+}

Figure 2 shows the phase behavior of decane and 0.182 *M* Alfoterra 145-4 PO sulfate/2.67 *M* IPA (10% Alfoterra 145-4 PO sulfate and 16% IPA, respectively) solutions when scanned with $AlCl_3$ and NaCl, respectively. The middle phase microemulsion began to appear at only 0.06 *M* aqueous $AlCl_3$ addition, while in the series with NaCl addition, no middle phase microemulsion appeared even at 0.30 *M* NaCl addition. About 25% of the free phase decane was solubilized into the middle phase at 0.06 *M* $AlCl_3$ addition, while less than 2.5% of the free phase decane was solubilized in the surfactant solution at 0.18 *M* NaCl addition. The high surface charge density of Al^{3+} makes it more effective than Na^+ for decreasing surfactant system HLB, and makes it possible for the

Table 2. Selected Properties of Contaminants

Contaminant	Structure	M.W.	Density (g/mL)	ACN/EACN
TCE (Trichloroethylene)	$CHCl=CCl_2$	131.4	1.463	−3.86[a]
Decane	$CH_3(CH_2)_8CH_3$	142.4	0.730	10
Tetradecane	$CH_3(CH_2)_{12}CH_3$	198.4	0.763	14

[a] From Ref. (18).

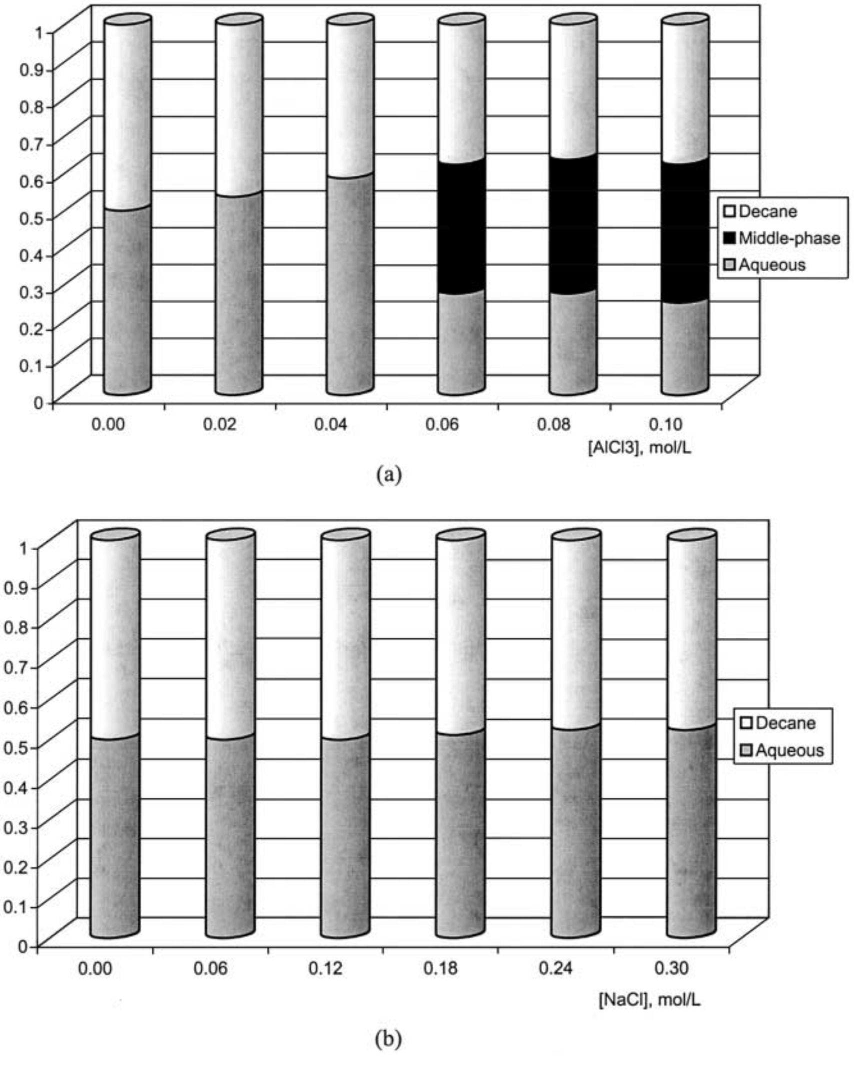

Figure 2. Comparison of the microemulsion phase behavior between decane and 0.182 *M* Alfoterra 145-4 PO sulfate/2.67 *M* IPA solutions at $AlCl_3$ and NaCl additions (a) Effect of $AlCl_3$ concentration; (b) Effect of NaCl concentration.

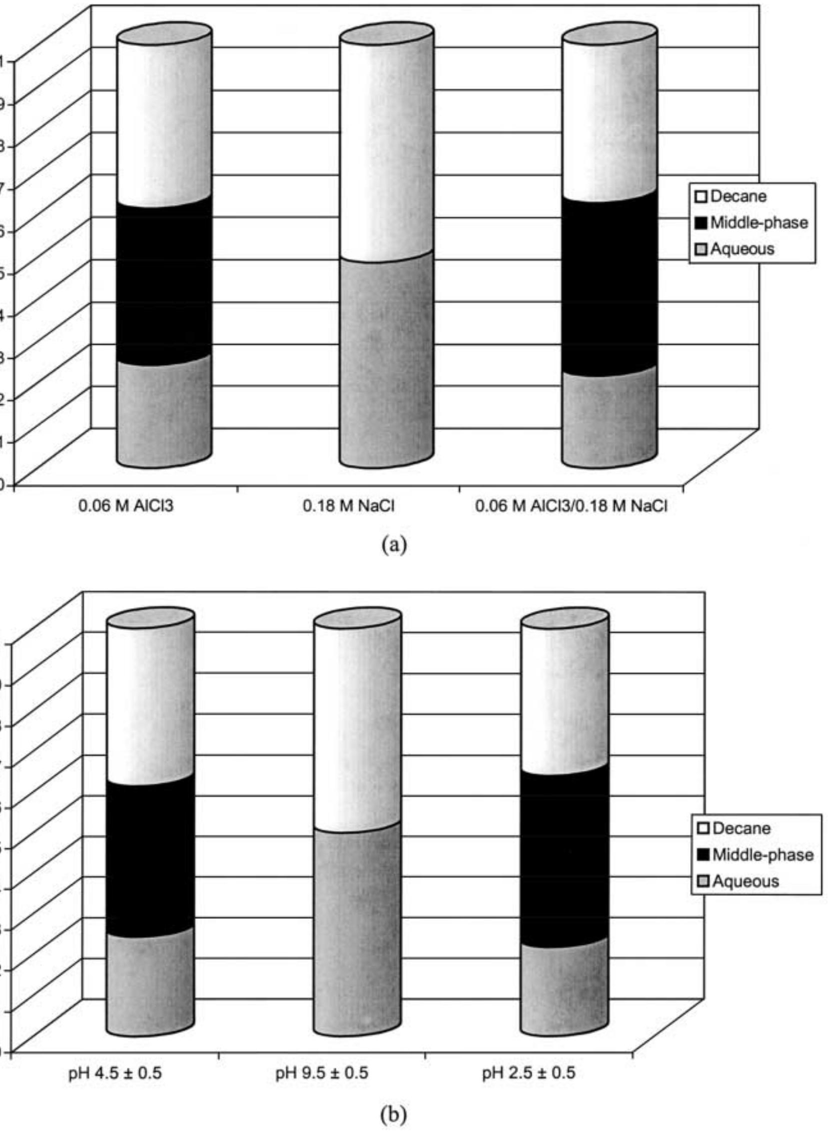

Figure 3. Transitions in microemulsion phase behavior between decane and 0.182 *M* Alfoterra 145-4 PO sulfate/2.67 *M* IPA solutions from electrolyte manipulation (a) Phase behavior with different electrolyte additions; (b) Transitions in phase behavior from sequential NaOH and HCl additions.

transition of the middle phase microemulsion back to a Winsor type I microemulsion after exchanging Al^{3+} with Na^+ through precipitation.

Figure 3(a) shows the phase behavior of decane with 0.182 *M* Alfoterra 145-4 PO sulfate/2.67 M IPA solutions with addition of 0.06 *M* $AlCl_3$, 0.18 *M* NaCl, and 0.06 *M* $AlCl_3$/0.18 *M* NaCl, respectively. Figure 3(b) shows the changes in phase behavior between decane and 0.182 *M* Alfoterra 145-4 PO sulfate/2.67 *M* IPA/0.06 *M* $AlCl_3$ solutions after adding 75 μL of 12 *M* NaOH solution (pH 9.5 ± 0.5), followed by addition of 113 μL of 8 *M* HCl (pH 2.5 ± 0.5). The phase behavior results from both figures were similar, and the middle phase volumes in the system containing both Al^{3+} and Na^+ were higher than those with Al^{3+} only. About 23% of the initial free phase decane was solubilized into the middle phase formed from 5.0 mL of surfactant solution, while less than 2.5% of the initial decane was solubilized in the type I microemulsion once Al^{3+} was exchanged with Na^+ brought about by precipitation. After Al^{3+} was re-dissolved with HCl addition, both Al^{3+} and Na^+ existed in aqueous solution and they collectively produced a greater effect on surfactant system HLB reduction than that achieved by 0.06 *M* Al^{3+} alone, resulting in an increase in middle phase volume (closer to the optimal condition). Thus, the phase behavior could be reversibly shifted between Winsor type III and type I with the precipitation and re-dissolution of Al^{3+}. After the replacement of Al^{3+} by Na^+ in aqueous solution, the middle phase went back to a Winsor type I microemulsion, whose contaminant solubilization capacity was relatively small, resulting in release of most of the initially solubilized contaminant. Figure 3(b) shows that after the precipitated Al^{3+} was re-dissolved, the volumetric portion of middle phase increased from 37 to 42%, as a result of the collective contributions of Al^{3+} and Na^+. The system was closer to an optimal one because of the existence of both cations.

Cation Exchange—Ca^{2+}

Figure 4 shows the phase behavior between tetradecane and 0.091 M Alfoterra 145-4 PO sulfate (5% Alfoterra 145-4 PO sulfate) solutions scanned with $CaCl_2$ and NaCl, respectively. The difference in phase behavior resulting from the addition of Ca^{2+} and Na^+ was less dramatic than that between Al^{3+} and Na^+, which can be explained by the smaller difference in surface charge density between the two. Calcium salts are more commonly used as electrolytes in surfactant system formulation than aluminum salts. Although the surface charge density of divalent Ca^{2+} is lower than that of trivalent Al^{3+}, there is still sufficient difference in the phase behavior of Ca^{2+} and Na^+ systems. This makes it possible to separate the contaminant solubilized in the middle phase by exchanging the Ca^{2+} in solution with Na^+ through precipitation of Ca^{2+} as an insoluble salt.

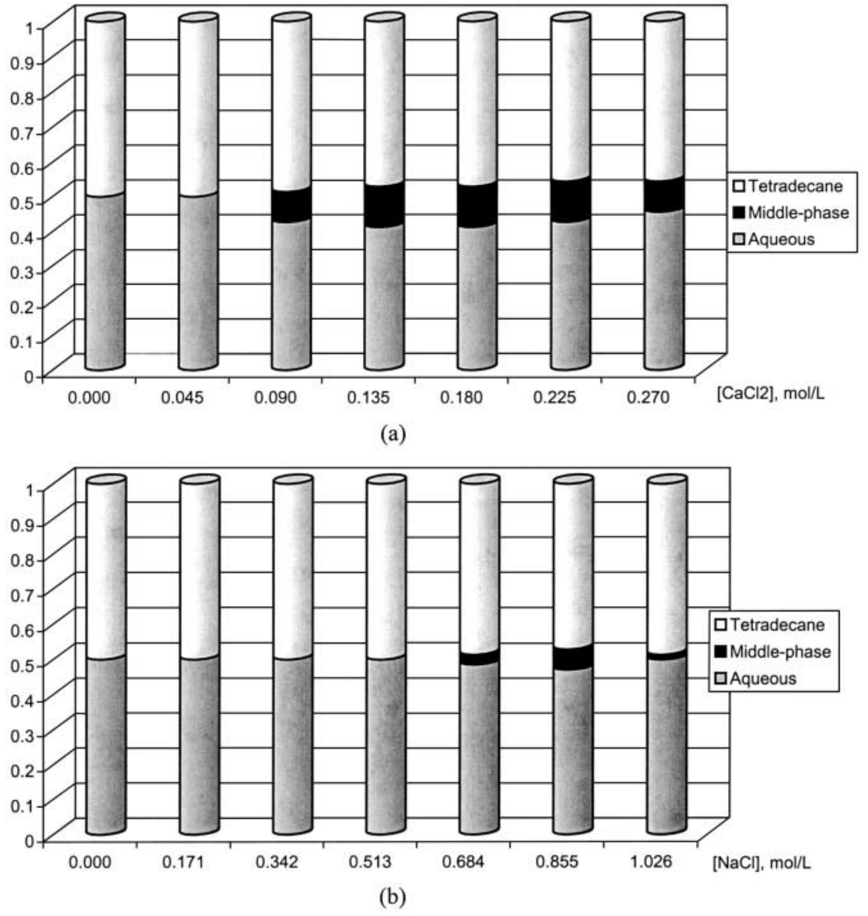

Figure 4. Comparison of the microemulsion phase behavior between tetradecane and 0.091 *M* Alfoterra 145-4 PO sulfate solutions at $CaCl_2$ and NaCl additions: (a) effect of $CaCl_2$ concentration; (b) effect of NaCl concentration.

Figure 5 shows the transitions in phase behavior between tetradecane and 0.091 *M* Alfoterra 145-4 PO sulfate/0.091 *M* $CaCl_2$ solution after added 230 μL of Na_2CO_3 solution to precipitate Ca^{2+}, followed by addition of 58 μL of HCl solution to re-dissolve the precipitated $CaCO_3$. After dissolution of Ca^{2+} by HCl, both Ca^{2+} and Na^+ existed together in aqueous solution, which 'pushed' the middle phase system closer to an optimal one, as observed previously with Al^{3+}.

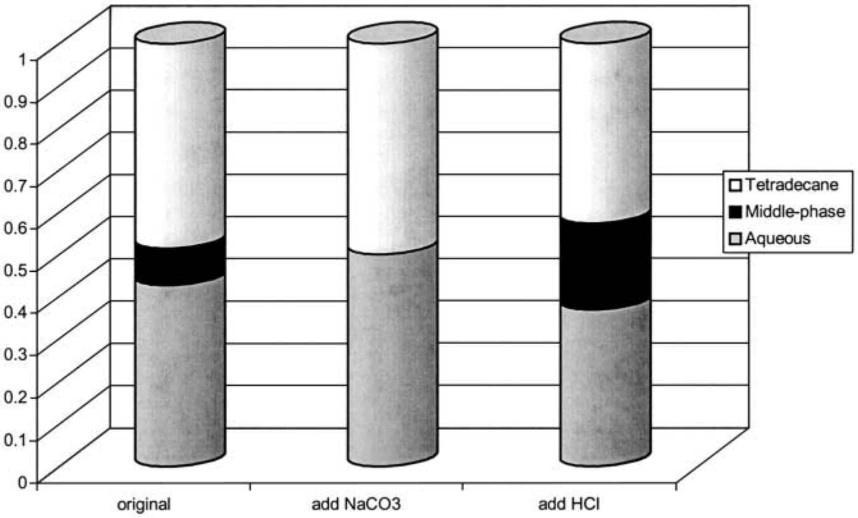

Figure 5. Transitions in phase behavior between tetradecane and 0.091 *M* Alfoterra 145-4 PO sulfate/0.091 *M* $CaCl_2$ solution from sequential Na_2CO_3 and HCl additions.

Organic Additive Transformation—Oleic Acid

Figure 6 shows the comparison of the salinity scan results for TCE and 0.107 *M* Aerosol MA/0.02 *M* oleic acid (4% Aerosol MA) solutions, and 0.107 *M* Aerosol MA/0.02 *M* sodium oleate solutions. Solubilization of TCE in 0.107 *M* Aerosol MA/0.02 *M* oleic acid solution increased with NaCl concentration in Winsor type I system region, resulting in increasing aqueous phase volume with solution salinity. A middle phase microemulsion began to appear at 0.171 *M* NaCl addition when neutral oleic acid molecules predominated in solution (pK_a of oleic acid is around 9.0 based on Ref. (19)). The microemulsion shifted to Winsor type II once the NaCl concentration was above 0.205 *M*. In the Winsor type II region, water was increasingly solubilized into the reverse micelles in TCE phase as aqueous salinity continued to increase (spurious experimental results were observed in Fig. 6a). On the other hand, when the oleic acid molecules existed predominantly as oleate anions in solution, 0.274 *M* NaCl was required for middle phase microemulsion to appear, and the microemulsion turned to Winsor type II at NaCl concentrations above 0.308 *M*. These results suggest that neutral oleic acid molecules can produce strong lipophilic interactions in the surfactant system and are more effective (in term of the surfactant solution electrolyte requirement) than the dissociated anions at enhancing the formation of middle phase microemulsions between Aerosol MA

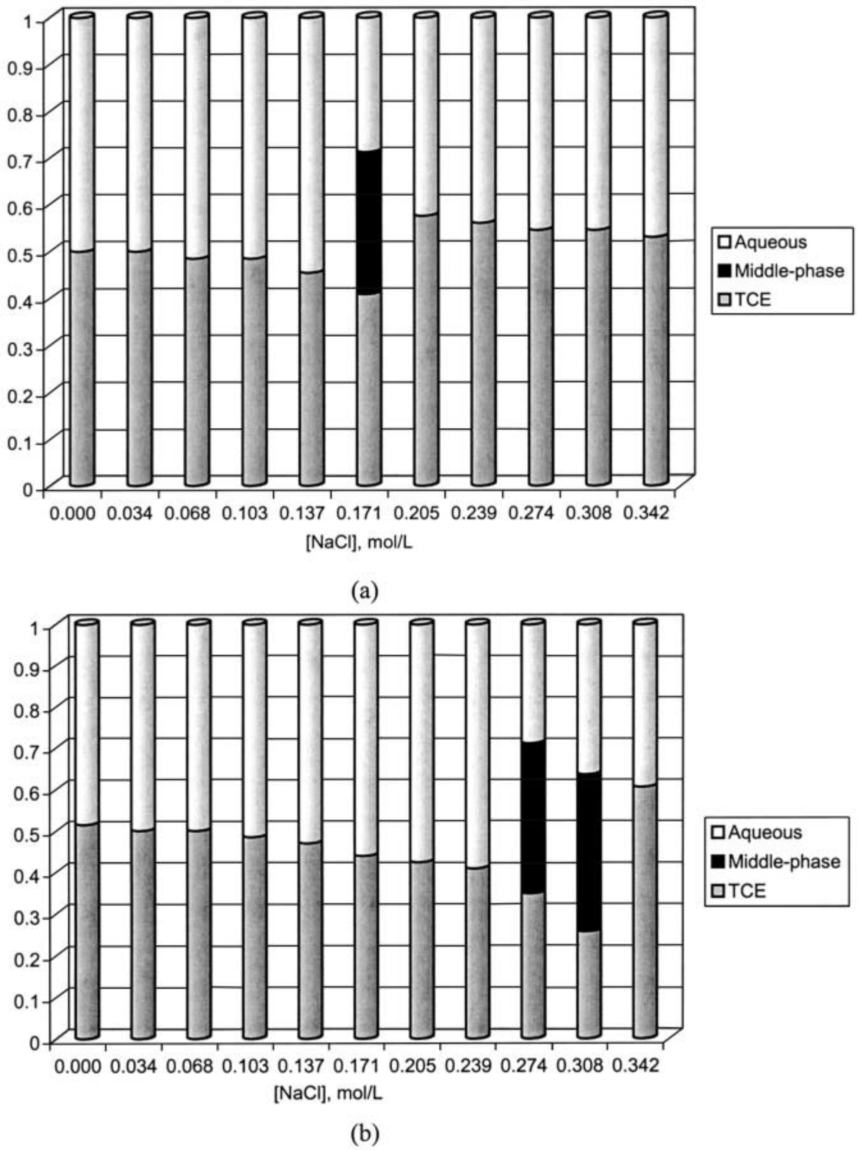

Figure 6. Comparison of the microemulsion phase behavior between TCE and solutions of 0.107 *M* Aerosol MA with 0.02 *M* oleic acid and 0.02 *M* sodium oleate at NaCl additions: (a) 0.107 *M* Aerosol MA/0.02 *M* oleic acid solution; (b) 0.107 *M* Aerosol MA/0.02 *M* sodium oleate solution.

solution and TCE. Oleic acid functioned as a lipophilic linker in this system and enhanced the interactions of surfactant hydrophobic tail groups with TCE molecules. On the other hand, the oleate anions behaved as co-surfactants in the system, which also enhanced the interactions between surfactant molecules and TCE by forming mixed micelles with Aerosol MA molecules. Because the neutral oleic acid molecules have a greater influence on the interactions between surfactant molecules and TCE molecules than their deprotonated counterparts, a transition from middle phase microemulsion back to Winsor type I is expected if the oleic acid molecules in the Winsor type III system can be deprotonated.

The pH of the microemulsion systems containing oleic acid was adjusted to study the feasibility of separating TCE solubilized in middle phase by 'pulling' the phase behavior back to Winsor type I through deprotonation of oleic acid. After adding 9 μL of 12 *M* NaOH solution into the middle phase system formed from 5 mL of TCE and 5 mL of 0.107 *M* Aerosol MA/0.02 *M* oleic acid/0.274 *M* NaCl solution, the Winsor type III microemulsion did not shift back to a type I, rather an increase in the middle phase volume was observed. Instead of deprotonating oleic acid molecules, it appears that the added NaOH increased the surfactant counterion (Na^+) concentration and 'pushed' the phase behavior towards a Winsor type II system. It is speculated that the oleic acid molecules distributed between the surfactant hydrophobic tail layers and TCE layers in the middle phase were not accessible to OH^- in the aqueous phase, preventing deprotonation of their acidic groups (–COOH). Even though the bi-continuous structure of a middle phase might be broken up into small portions upon shaking, each portion kept its structural integrity and did not allow access of OH^- to oleic acid molecules between the oil layers and the surfactant hydrophobic tail layers. As a result, unlike the scenario where oleic acid was already dissociated before the introduction of organic liquid, the introduction of NaOH after the existence of middle phase microemulsion could not affect the microemulsion phase behavior. Solution pH measurements also supported this conclusion, which showed a pH of 12.5 ± 0.5 in the aqueous phase after NaOH addition while that of middle phase was still around 7.

In contrast, it was found that HCl addition clearly shifted the microemulsion phase behavior between TCE and 0.107 *M* Aerosol MA/0.02 *M* sodium oleate solutions at various salinities (data not shown), indicating that HCl was able to protonate the oleate anions and transform them to the neutral form in both Winsor type I and type III microemulsion systems. In Winsor type I systems, oleate anion existed as a co-surfactant and formed mixed micelles with Aerosol MA molecules. The head group ($-COO^-$) of oleate anion was in contact with the aqueous phase, allowing it to be accessed by aqueous H^+. In Winsor type III systems, the oleate anions packed their molecules in parallel with those of Aerosol MA in the middle phase to form surfactant layers: head groups contacting water layers while tail groups contacting TCE layers. It is believed

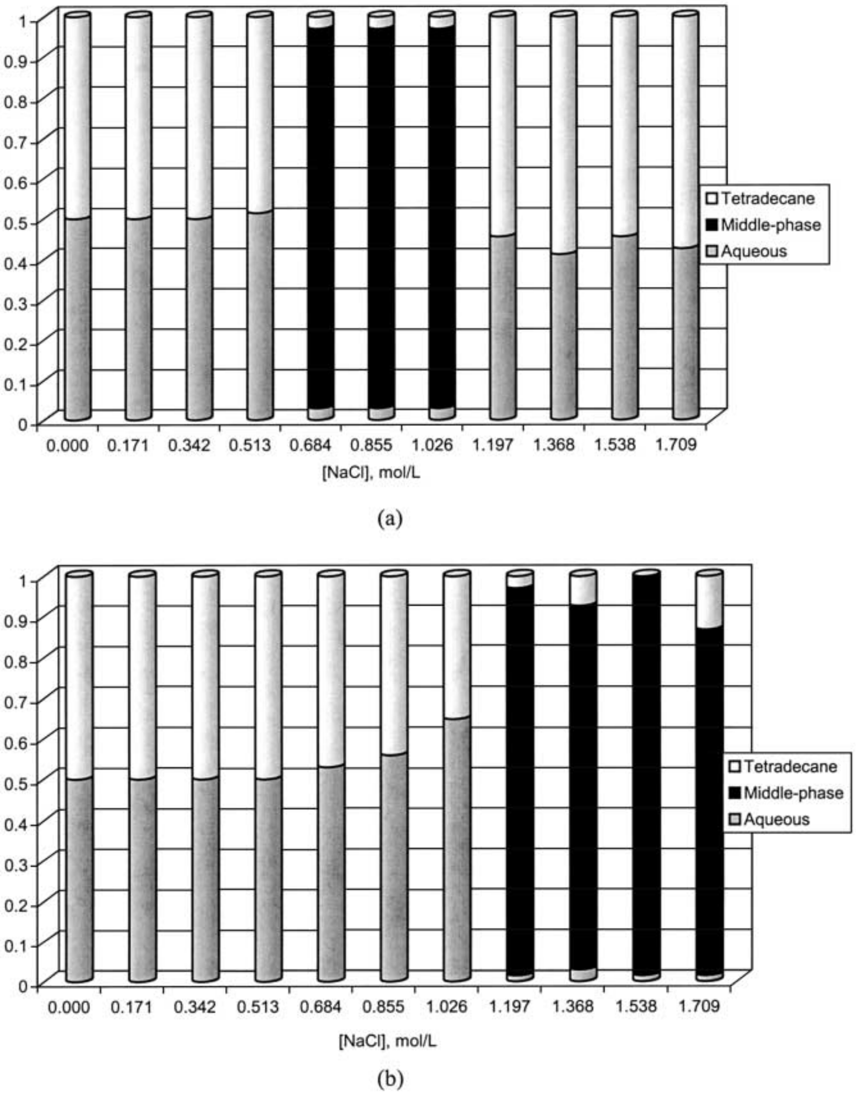

Figure 7. Comparison of the microemulsion phase behavior between tetradecane and solutions of 0.091 *M* Alfoterra 145-4 PO sulfate with 0.02 *M* oleic acid and 0.02 M sodium oleate at NaCl additions: (a) 0.091 *M* Alfoterra 145-4 PO sulfate/0.02 *M* oleic acid solution; (b) 0.091 M Alfoterra 145-4 PO sulfate/0.02 *M* sodium oleate solution.

that during shaking, aqueous H^+ was able to diffuse into the water layers in the middle phase and subsequently protonated the head groups ($-COO^-$) of oleate anions. The protonated oleic acid molecules became neutral and migrated to the hydrophobic regions (TCE layers and surfactant tail layers) in the system and started to function as linkers. The interactions between Aerosol MA and TCE molecules were greatly enhanced by these linkers, which resulted in transitions of the microemulsion phase behavior. However, instead of shifting the microemulsion from a Winsor type III to a type I, the protonation of oleate anion 'pushed' the phase transition towards a type II, and this reaction was difficult to reverse in middle phase systems because of the residing location of the neutral oleic acid molecules.

Figure 7 shows the comparison of salinity scan results for tetradecane and 0.091 *M* Alfoterra 145-4 PO sulfate/0.02 *M* oleic acid (5% Alfoterra 145-4 PO sulfate) solutions, and 0.091 M Alfoterra 145-4 PO sulfate/0.02 *M* sodium oleate solutions. Middle phase microemulsion began to appear at 0.684 *M* NaCl addition when the neutral oleic acid molecules predominated in solution, and the phase behavior shifted to Winsor type II once the NaCl concentration was above 1.026 *M*. On the other hand, when the oleic acid molecules existed predominantly as dissociated anions (oleate) in solution, 1.197 *M* NaCl was required to form a middle phase between tetradecane and the 0.091 M Alfoterra 145-4 PO sulfate solution. These results also indicate that the neutral form of oleic acid was more effective than the oleate anion at enhancing the formation of middle phase microemulsion between surfactant solutions and contaminants. Attempts to shift the middle phase microemulsion containing oleic acid towards a Winsor type I microemulsion by pH adjustment were also not successful. On the other hand, adding HCl to microemulsion systems containing oleate anions caused the phase behavior to shift towards a Winsor type II microemulsion. All these results consistently show that the transformation of oleic acid in middle phase microemulsions is very difficult, while oleate anions can be protonated again even when they are in middle phases. Therefore, the existing form (neutral or anionic) of oleic acid determines its distribution and function in microemulsion systems, as well as the potential of being transformed.

CONCLUSIONS

Using phase transitions to separate contaminant solubilized in middle phase microemulsions was studied by adjusting the hydrophilic and lipophilic interactions in the systems. High surface charge density polyvalent cations were exchanged with equivalent amounts of low surface charge density monovalent cation by cation precipitation. This exchange shifted microemulsion systems from Winsor type III to type I, resulting in the release of excess contaminant mass because of the much smaller contaminant solubilization capacity of the type I system. The precipitation of polyvalent cations was reversible and could be manipulated to separate contaminant solubilized in middle phase microemulsions and reuse the surfactant-containing aqueous phase. It was not possible to separate contaminant solubilized in middle phase microemulsions promoted by a lipophilic linker (oleic acid) by just adding NaOH solution. Oleic acid molecules distributed between the surfactant hydrophobic tail layers and contaminant layers in middle phase microemulsions, and appeared not to be accessible by aqueous OH^- for neutralization. On the other hand, oleate anion functioned as a co-surfactant and could be readily protonated to oleic acid even in middle phase systems because the functional group ($-COO^-$) was always in contact with water. This research thus demonstrates that Winsor type III surfactant systems containing polyvalent cations can be efficiently decontaminated by shifting them to type I systems, which can be accomplished by exchanging the polyvalent cations with monovalent counterparts through precipitation.

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