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Separation of Organic Compounds from Surfactant Solutions: A Review

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Abstract: This review summarizes the recent development in separation of emulsified organic compounds from surfactant solutions for surfactant reuse and/or surfactant-contaminant disposal. Three major principles have been employed for separating organic compounds and/or surfactants from aqueous solutions, namely, organic compound inter-phase mass transfer, surfactant micelle removal, and manipulation of surfactant solution phase behavior. Details of these principles and their applications are discussed, with the advantages and limitations of each separation method compared. Separation based on mass transfer of the organic compounds into a secondary phase is currently more practical than the others. Finally, two major issues requiring further research are identified.

Keywords: Surfactant, organic compound, solubilization, separation, surfactant reuse

SURFACTANT PROPERTIES AND PHASE BEHAVIOR

Surfactants are amphiphilic, surface-active molecules containing both hydrophilic and hydrophobic groups. The amphiphilic nature of surfactant

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molecules causes them to accumulate at interfaces, with the hydrophilic head and hydrophobic tail in the polar and nonpolar phases, respectively. Surfactants are typically classified by the nature of their head group, which can be positively charged (cationic), negatively charged (anionic), both positive and negatively charged (zwitterionic), or uncharged (non-ionic) (1, 2). A phenomenon unique to surfactants is the self-assembly of molecules into dynamic clusters called micelles above a certain concentration, known as the critical micelle concentration (CMC). In the micelles, surfactant molecules are oriented such that their hydrophilic head groups shield the hydrophobic tail groups from the water environment. The interior of micelles acts as an organic pseudo-phase into which organic compounds can be partitioned, and the apparent solubilities of hydrophobic organic compounds can be significantly increased. Because of the size and structural limitation of the micellar cores, a maximum solubilization capacity exists (3, 4); nonetheless, various microemulsion phases can be exploited to further maximize the solubility enhancement (5–8).

For a given organic liquid, the ability of surfactants to produce optimal microemulsions is characterized by a parameter called the hydrophile-lipophile balance (HLB). Higher HLB values indicate that surfactants prefer the water phase, and vice versa. As illustrated in Fig. 1, the surfactant becomes more lipophilic and the system transitions in the order of Winsor

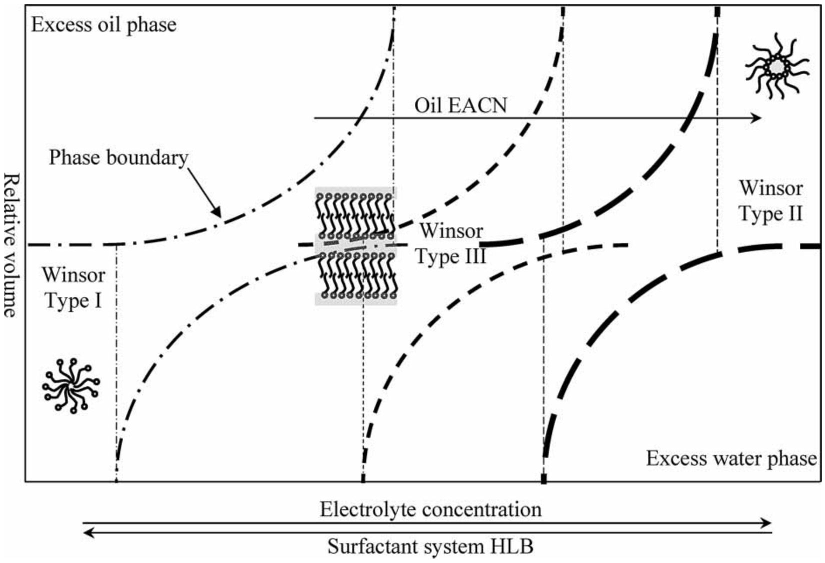

Figure 1. Effect of electrolyte addition on surfactant system HLB and microemulsion phase behavior between an ideal ionic surfactant solution and organic compounds with increasing hydrophobicity (which can be indicated as equivalent alkane carbon number, or EACN, adapted from (11)).

Type I—III—II microemulsion when the surfactant system's HLB decreases (3, 9–11). In a Winsor Type I system, the surfactant is very water soluble and is in the form of oil-swollen micelles in the aqueous phase. In the Winsor Type II system, the surfactant is very oil soluble and exists predominantly in the form of water-swollen reverse micelles in the oil phase. The Winsor Type III system has nearly equal affinity for both phases. This forms a new phase, the middle-phase microemulsion, which has a bicontinuous structure and contains almost all of the surfactant and large quantities of the organic compound and water (2). Winsor Type III microemulsion, where the interfacial tension (IFT) is minimum and the solubilization is maximum, is considered the optimal phase behavior. While an ionic surfactant is assigned a single HLB value, electrolytes or organic additives impact the effective HLB value of the surfactant solution. Increasing aqueous phase salinity causes the surfactant to be salted out into the organic phase, which translates into a lipophilic shift (i.e., decreasing the surfactant system HLB). Therefore, as the salinity of a surfactant solution increases, the microemulsion will shift in the order of Winsor Type I—III—II. As the hydrophobicity of organic liquids increases, more and more lipophilic (lower HLB) surfactant systems are required to form the optimal microemulsion (10).

Besides electrolytes, organic additives (including alcohols and hydrotropes) can also help to optimize microemulsion formation. Alcohols play a two-fold role in microemulsion formulation: adjusting the surfactant partitioning between aqueous and organic phases (as co-solvent), and stabilizing the microemulsion by preventing the formation of rigid phases (as co-surfactant) (12). Organic hydrotropes, such as short-chain carboxylic acids, can also enhance the interactions between contaminant molecules and those of the surfactant and thus promote the formation of middle phase microemulsions (12).

SURFACTANT-BASED SUBSURFACE REMEDIATION TECHNOLOGIES AND SEPARATION NEEDS

While pump-and-treat is a common technology for cleaning up groundwater aquifers contaminated by non-aqueous phase liquids (NAPLs) such as gasoline or tetrachloroethylene, it is inefficient because of the low aqueous solubilities of the organic contaminants. Surfactant enhanced aquifer remediation (SEAR) has emerged as a promising technology to expedite remediation of subsurface sites contaminated with NAPLs (1, 3, 13–15). For this remediation scheme (Fig. 2), the surfactant solution is injected below ground to enhance the extraction of the contaminant. Once the surfactant-contaminant stream comes above ground, separation processes are necessary for either re-injection of the surfactant solution or disposal of the waste stream. Due to the enhanced solubilization of organic contaminants in surfactant solutions and the reduction in IFT between organic contaminants and the aqueous phase, the remediation time can be dramatically reduced compared

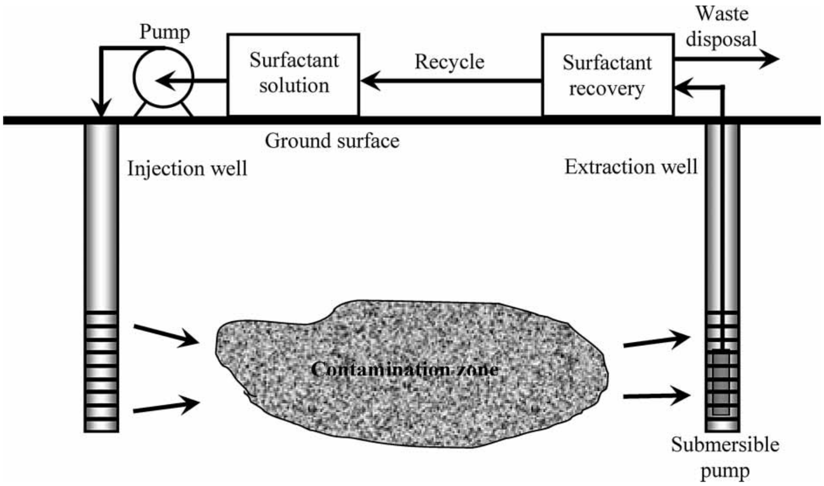

Figure 2. Schematic illustration of surfactant enhanced aquifer remediation (SEAR). SEAR is an aggressive technology for source removal and can recover the vast majority ($>$95%) of NAPL from a source zone in a relatively short time period. System economics motivates adaptation of separation processes for surfactant recovery and reuse, which is especially important for multiple pore volume ($>$3 to 5 pore volumes) surfactant flushes.

to traditional pump-and-treat remediation. 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 a free phase oil (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 enhanced dissolution (enhanced solubilization mechanism). Historically, the solubilization mechanism has been preferred for dense NAPLs in an effort to minimize downward migration potential (16), while the recovery by mobilization and solubilization into a middle-phase microemulsion has been preferred for light NAPLs (17). More recently, supersolubilization and gradient systems have been introduced to further improve the efficiency of SEAR for dense NAPL remediation (6, 8, 18, 19).

Historically, the economics of surfactant-based remediation technologies benefited from materials separation and recycle of surfactant (20–27). Separation of organic compounds from surfactant solutions is necessary to reuse the surfactant solution and to lessen the demand on waste disposal in implementing SEAR, both of which improve system economics (23–25, 27). While only the micellar-solubilized contaminant needs to be removed from the water phase if the surfactant solution is to be re-injected, both contaminant and surfactant may require removal from the waste stream before being discharged into a wastewater treatment plant. More recently, development of systems based on lower surfactant concentrations ($<$1 wt.% versus 4 to 8%) and requiring fewer pore volumes (1.5 to 2 versus 6 to 10 pore volumes or more) has reduced, but not always eliminated, the value of surfactant recovery and reuse in SEAR (6, 8, 19).

Surfactant-based processes are also widely used in many other industrial and environmental applications; surfactant-contaminant separation may also be desirable in a number of these technologies. Since the early 1970s, surfactant systems have been evaluated for enhanced oil recovery (EOR). The application of surfactant solutions in subsurface remediation evolved from knowledge garnered during EOR research (13). Surfactants can also be used in ex situ soil washing and cleaning of oil well drill cuttings (28–30). Micellar-enhanced ultrafiltration (MEUF), which involves adding surfactants to aqueous streams followed by ultrafiltration, is an alternative separation process for removing organic solutes from water (31–35). Cloud point extraction using nonionic surfactants has been used in pre-concentrating organic solutes in aqueous solutions and in removing organic compounds from wastewater (36–42). Significant cost savings of these processes can be achieved by reusing the surfactants after economically separating the emulsified organic compounds from the surfactant solutions.

In the last two decades, with great advances in SEAR research and implementation, significant research effort has focused on removing organic compounds from surfactant solutions. Surfactant-contaminant separation methods that have been developed are summarized in Table 1. This review intends to summarize the research progress in separating organic compounds from surfactant solutions and to identify areas requiring further research. In general, several fundamental principles are employed in separating organic compounds from surfactant solutions, namely, organic compound inter-phase mass transfer, surfactant micelle removal, and manipulation of surfactant solution phase behavior. Details on these principles and their applications are discussed in the following sections.

SEPARATION BY INTER-PHASE MASS TRANSFER

Organic compound separation from micellar solution often utilizes preferential partitioning of the organic compound into a second phase, which can be gaseous or liquid. Important considerations in this approach are the equilibrium partitioning of the organic compound between this second phase, water, and the micellar pseudo-phase, along with the inter-phase mass transfer rate. Technologies based on this approach are described below.

Air Stripping and Related Technologies for Removing Semi-Volatile to Volatile Organic Compounds

Volatile organic compounds (VOCs), that is, compounds with high Henry's Law constants, readily partition into the gas phase. Consequently, air stripping and

Table 1. Summary of the advantages and limitations of existing surfactant-contaminant separation methods

Method	Applicable conditions	Advantages	Limitations
Air stripping	Volatile organic compounds	• Highly efficient • Low equipment cost	• Significant foaming can occur (hollow fiber membrane eliminates this, but adds cost) • Does not work well for concentrated surfactant solutions
Flash vacuum stripping and vacuum distillation	Compounds can be semi-volatile	• Works well for concentrated surfactant solutions • Works for compounds that are not highly volatile	• Significant foaming can occur • High equipment cost • Requires vacuum • May require heating
Pervaporation	Volatile organic compounds	• Foaming is eliminated	• Relatively high equipment cost
Solvent extraction	Compounds can be nonvolatile	• Works well for nonvolatile organic compounds • Highly efficient	• Relatively high cost for solvent • Requires solvent disposal
Surfactant precipitation by counterions	Ionic surfactants	• Low cost • Operationally convenient	• May require further treatment to remove the counterions

Surfactant precipitation by cooling	Ionic surfactants with Krafft temperatures near room temperature	•Low cost •Operationally convenient •Recycled surfactant is readily reused	•Surfactants must have Krafft points near room temperature
Adsorption on ion exchange resin	Ionic surfactants	•Removes both surfactants and organic compounds (assuming organic-based resin) •Works well for high surfactant concentration streams	•Relatively high cost for resins •Surfactants cannot be recovered
Activated carbon adsorption	Polishing step after pretreatment	•Removes both surfactants and organic compounds •Works for all types of surfactants and organic compounds	•Relatively high cost for activated carbon •Cannot handle streams with high surfactant concentrations
Reverse micellar extraction	Highly hydrophobic organic compounds	•Removes both surfactants and organic compounds into the solvent phase	•Separation of organic compounds from surfactants may be difficult
Phase transition by exchanging cations	Anionic surfactant systems with ultralow IFT and polyvalent cations	•Effective in changing a Winsor Type III microemulsion system to a Type I system	•Limited to Winsor Type III surfactant systems •Solubilized organic compounds are not removed from surfactant solutions

related technologies (e.g., vacuum stripping) can be used to remove VOCs from surfactant solutions. Air-stripping systems work by contacting the surfactant solution with contaminant-free air to promote partitioning, while creating a large air-water interfacial area, which facilitates the mass transfer of organic compounds from the solution to the air phase. Both supported-area (i.e., packing materials) devices and unsupported-area (i.e., trays) devices can be used for VOC removal in air stripping (43). Packed-tower strippers have been commonly used for removing VOCs from surfactant solutions (19, 21, 44–48), while sieve-tray air stripping systems have also been evaluated in laboratory and field studies (27, 49, 50). In addition to traditional air stripping towers or tray strippers, stripping techniques based on hollow fiber membranes have also been developed (26, 48, 51). Air-liquid interface is established in the pores ranging from 30 to 50 nm that are typically present in the polypropylene hollow fibers (21, 48). Use of the hollow fiber membrane reduces foaming problems, which is common in packed tower and tray air strippers (27), although foam formation may still occur at very high liquid loading rates (48, 51). Weeping of the surfactant solution across the membrane in air stripping can be effectively prevented by back pressure regulation (21, 51).

Besides air stripping, vacuum processes can also be used to remove VOCs; these also work well for concentrated surfactant solutions (47, 52, 53). Flash vacuum stripping can be carried out in a packed column or tray stripper, but instead of using air flow, a vacuum is used to transfer the contaminant from the liquid to the vapor phase. Flash vacuum distillation is similar to flash vacuum stripping except the surfactant stream is heated to raise the vapor pressures of the contaminants (25). Application of vacuum allows these technologies to be applied for contaminants that are less volatile. However, significant surfactant foaming can occur and their equipment cost is much higher than air stripping.

Another process similar to air stripping is pervaporation, which is a membrane-based process for the separation of liquid mixtures (54). A liquid feed is brought to the upstream side of a nonporous polymeric membrane, which swells in contact with the feed. The components of the feed absorb into the membrane, permeate through the membrane, and evaporate into a gas phase on the downstream side of the membrane. Pervaporation has been evaluated in laboratory and pilot studies (55–58), and successfully implemented in field demonstrations to remove VOCs from surfactant streams without affecting the performance of the surfactant solutions (59, 60).

Solvent Extraction for Removing Low-Volatility Organic Compounds

Since air-stripping and related technologies are not effective for removing low-volatility organic compounds from surfactant solutions, an organic liquid can be used instead of a gas phase as the partitioning phase. This approach, known as solvent extraction or liquid-liquid extraction, involves introducing a solvent to the surfactant solution so that the organic compound will transfer from the surfactant solution into the solvent phase. Solvent extraction has been used to remove semi- and nonvolatile organic compounds from surfactant solutions in both laboratory and field studies (22, 44, 61, 62). Because solvent extraction also relies on mass transfer, it is not possible to achieve complete removal of the contaminants from the surfactant solution. The solvent extraction process can be complicated by emulsification of the extraction solvent by the surfactant solution, and highly hydrophobic solvents are often required to avoid this (22, 26). Similar to air stripping, hollow fiber membranes can be used in continuous solvent extraction. The hollow fiber membrane pores are filled by the extraction solvent, which is sparingly soluble in the surfactant solution. Despite this, hollow fiber membrane units have been demonstrated to effectively eliminate emulsification of extraction solvents by surfactant solutions while maintaining excellent extraction efficiency (22, 26, 62).

Impact of Micelles on Equilibrium and Kinetics of Organic Compound Inter-Phase Mass Transfer

Numerous studies have shown that the presence of micelles reduces the aqueous activity and thereby the driving force for the partitioning of organic compounds into the gas or solvent phase (21, 22, 26, 27, 46, 61, 63–68). Because the organic molecules are predominately solubilized within the hydrophobic cores of micelles, the organic molecules that are actually water-solubilized are only a small fraction of the total. The activity of the organic compound in surfactant solutions is solely determined by the extramicellar (water-solubilized) organic molecules, while the micellar pseudo-phase acts as a competing sink for the partitioning of the organic compound (26, 63–66). Figure 3 schematically illustrates the distribution of surfactant and organic molecules in air stripping and solvent extraction systems. The aqueous surfactant monomer concentration is constant above the surfactant CMC, and the gas phase is surfactant-free. Partitioning of ionic surfactant monomers into the solvent phase is negligible, while greater surfactant partitioning into the solvent phase is expected for nonionic surfactants. Within the aqueous solution, an organic compound exists in both extramicellar and micellar-solubilized forms, whereas it exists as vapor or solvent-solubilized molecules in the air and solvent phases, respectively. Distribution of the organic molecules among the water phase, micellar pseudo-phase, and the gas or solvent phase are related by the respective partitioning processes. Solubilization of the solvent molecules into the micellar pseudo-phase also occurs but will be negligible when the solvent is selected properly (22, 26).

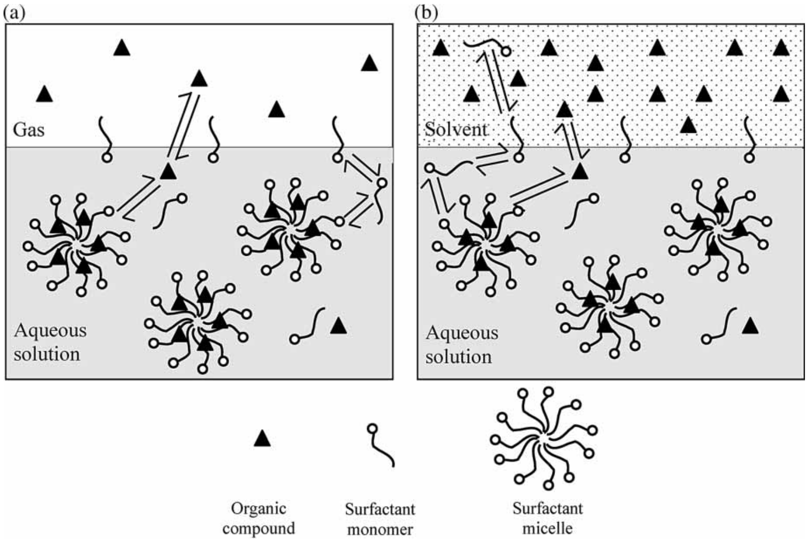

Figure 3. Distribution of surfactant and organic compound molecules in (a) gas-aqueous solution system, and (b) solvent-aqueous solution system, which correspond to the scenarios of air stripping and solvent extraction, respectively.

The molar solubilization ratio (MSR) that describes the organic solubilization capacity of a micellar surfactant solution is defined as (3, 4, 26, 69, 70):

$$MSR = \frac{C_{mic} - C_w}{C_s - CMC}$$

where C_{mic} is the amount of organic compound solubilized for a given surfactant concentration (all concentrations are referenced to the volume of the solution), C_w is the organic compound's water solubility, and C_s is the total surfactant concentration. Partitioning of the organic compound between water and micellar pseudo-phase can be described by a micelle-water partition coefficient (K_{mw}) as (3, 4, 26):

$$K_{mw} = \frac{X_m}{X_w}$$

where X_m is the mole fraction of micellar-solubilized organic compound in the micellar pseudo-phase and X_w is the mole fraction of extramicellar organic compound in the water phase. K_{mw} has been observed to be independent of the total aqueous contaminant concentration and can be estimated from MSR as (3, 26, 71):

$$K_{mw} = \frac{MSR}{1 + MSR}\left(\frac{55.556}{C_w}\right)$$

Partitioning into the micellar cores significantly reduces the fraction of the organic molecules that reside in extramicellar form, which is the fraction readily partitions into the gas or solvent phase. The micellar-solubilized contaminant molecules are shielded from the solvent phase by the surfactant micelles, and the micellar pseudo-phase functions as a competing sink with the solvent phase for partitioning of the organic contaminant. Consequently, the efficiency of air stripping and solvent extraction is reduced, as has been observed in laboratory and field studies (21, 22, 26, 27, 51, 61). In solvent extraction, solubilization of the extraction solvent in the micelles may further increase the affinity of the micellar pseudo-phase for the organic compounds and negatively impact the extraction efficiency (26). In both cases, this competitive partitioning must be accounted for in designing the separation process, and when this is done correctly the separation process will achieve the design goal (51).

Besides reducing the activities of organic compounds, the presence of micelles has the potential to hinder their inter-phase mass transfer rates from surfactant solutions to gas or solvent phase. Due to reduction in surface tension, the presence of surfactant allows easy creation of interfacial area, which is beneficial for the mass transfer process. However, the fact that organic molecules are mostly solubilized within surfactant micelles may also create an extra resistance to the interfacial mass transfer (72). It is believed that only the extramicellar organic compound can volatilize, and because most of the organic molecules reside in the micelles, an additional mass transfer step (from inside the micelle to the water phase) is required (21). Reduction in solute mass transfer coefficient as compared to that for pure water in the presence of surfactants has been reported in solvent extraction systems (61, 72–76). In pervaporation, the solute has to diffuse through the nonporous membrane, which is much slower compared to the mass transfer in hollow fiber membrane-based separation processes (77). Reduction of VOC mass transfer from surfactant solutions during pervaporation has been attributed to the increase in the liquid viscosity that increases the liquid-side-boundary-layer mass transfer resistance (also known as concentration polarization), and the reduction in the effective extramicellar concentration due to the partitioning of the VOC into the surfactant micellar phase (55, 56). Vibrating pervaporation has been developed to reduce the concentration polarization during VOC removal from surfactant solutions (58, 60). A recent theoretical analysis based on results of equilibrium measurements in micellar systems and pervaporation experiments found that VOC mass transfer is enhanced considerably by diffusing micelles, which transport the solubilized VOC molecules in the direction of the membrane surface (78).

SEPARATION ACHIEVED BY SURFACTANT MICELLE REMOVAL

Both air-stripping and solvent extraction remove the organic compound out of surfactant micelles while leaving the micelles intact in aqueous solution.

On the other hand, if the surfactant micelles are depleted from the solution, the organic compound will become supersaturated and will phase separate from the aqueous phase. The organic compound concentration in the aqueous phase will be at its water solubility, coexisting with surfactant monomers (at the CMC), once all the micelles are removed, and discharge of the decontaminated stream may be possible. Micelle removal leads to simultaneous reduction in the surfactant concentration and phase separation of the micellar-solubilized organic compound.

Surfactant Precipitation by Counterions and Cooling

Precipitation of surfactants in aqueous solution is a phenomenon of great practical importance in many applications, such as detergency and petroleum production (79, 80). The concept of precipitating the surfactant from the solution, leaving organic solute dissolved in solution or as a separate phase, is attractive because the solute does not need to be volatile (35, 81, 82). Ionic surfactants can be precipitated by adding an ion having a charge opposite to that of the surfactant (counterion) or by decreasing the solution temperature below its Krafft temperature. The precipitation can be viewed as a competition process for the monomeric surfactant molecules to form micelles (79, 80). As the surfactant monomer precipitates, the monomer concentration is replenished from the micelles, thereby reducing and eventually depleting the micelles. Precipitated surfactant can be separated from the solution phase and reused, and the micellar-solubilized organic compound can also be separated from aqueous solution.

Studies have shown that counterion precipitation of ionic surfactants from aqueous phase can be described by a solubility product relationship between the surfactant monomers and the counterions after correcting their activities properly (35, 83–85). Counterions used for precipitating anionic surfactants can be monovalent (e.g., Na^+, K^+) (81, 82, 84), divalent (e.g., Ca^{2+}) (81, 86–88), trivalent (e.g., Al^{3+}) (81), or cationic surfactants (e.g., quaternary ammonium polyelectrolyte) (79, 80, 85). The rate of precipitation is on the order of several minutes to reach an equilibrium for pure anionic surfactant precipitated by Ca^{2+}, but can be longer (e.g., precipitation of an anionic surfactant by a cationic surfactant takes about 30 minutes) (79, 80, 88). Multivalent cations are more effective at precipitating anionic surfactant molecules, but the precipitated surfactant requires further treatment to be reused (35).

The temperature at which the aqueous solubility of an ionic surfactant equals the CMC is referred to as the Krafft temperature. Below the Krafft temperature, micelles will not form and the surfactant solution will have no solubilization potential. Precipitation of anionic surfactants by decreasing temperature is similar to the case of precipitation caused by the counterions (79, 80). Wu et al. reported a surfactant recovery scheme of precipitating surfactant by cooling the solution below the Krafft temperature (35). It was found that relatively little organic solute co-separated with the surfactant or adsorbed on the surfactant crystal (35). Precipitation of ionic surfactants by lowering the solution temperature below their Krafft temperatures is operationally convenient and the precipitated surfactants can be reused readily. On the other hand, for this approach to be economically viable, the surfactants should have Krafft temperatures near room temperature to minimize energy consumption associated with the cooling process.

Surfactant Removal by Ion Exchange and Adsorption

Adsorption on ionic exchange resins is another method for removing surfactant monomers and thus micelles from aqueous solutions. Organic ion exchange resins are composed of high molecular weight polyelectrolytes that can exchange their mobile ions for ions of similar charge from the surrounding medium. Ion exchange resins have a fixed number of sites that set the maximum quantity of exchange per unit of resin. Because of the presence of ion exchange sites and porous polymeric matrix on these resins, surfactant adsorption can be motivated by electrostatic attractions and/or hydrophobic interactions (89–93). Head and tail group properties of the surfactant molecules, along with resin structure and particle size can affect their uptake (94). Depending on the predominance of the electrostatic or hydrophobic interactions, the adsorption of surfactant molecules may increase or decrease with increasing electrolyte concentration (93, 95). Kawabata and Morigaki reported that the anionic surfactant sodium dodecylbenzenesulfonate adsorbed on an anion-exchange resin could be completely removed by organic solvents without adding electrolyte (96). A recent study showed that anionic surfactants were almost irreversibly adsorbed by anion exchange resins and recovery of the adsorbed surfactant was not practically feasible (94). It was also observed that the micellar-solubilized organic compounds were simultaneously removed with the surfactant uptake, which eventually partitioned into the resin gel phase matrix (94).

Activated carbon, which has been widely used in removing organic contaminants from drinking water, can also be used for removal of organic compound and surfactant from aqueous solutions (23, 50). While activated carbon adsorption can be used as a polishing step after pretreatment with other technologies (50), it is not practical to use activated carbon to treat waste streams containing high concentrations (>500 mg/L) of surfactants (23). Because of the poor selectivity for surfactant and organic compound molecules, separation methods based on ion exchange and adsorption are not good choices for surfactant recovery and reuse. Instead, they are well suited for decontamination of the waste surfactant streams by simultaneously removing the surfactants and organic compounds. It should also be noted that surfactant removal by ion exchange and adsorption can be slower compared to other separation processes when the adsorption requires intraparticle diffusion into the sorbent.

SEPARATION BY MANIPULATING SURFACTANT SOLUTION PHASE BEHAVIOR

As discussed in the Introduction, the microemulsion formed by an organic liquid with a surfactant solution transitions in the order of Winsor Type I—III—II when HLB of the surfactant system increases. Also, HLB of a surfactant system is impacted by electrolytes and organic additives. The phase behavior of surfactant solutions can be taken advantage of to separate the emulsified organic compounds.

Surfactant and Organic Compound Removal by Reverse Micellar Extraction

As shown in Fig. 1, for highly hydrophobic organic compounds (i.e., having high equivalent alkane carbon numbers, or EACNs), surfactant systems with very low HLB values are required to efficiently solubilize them or to form the optimum microemulsions (10). A recent study suggested that highly hydrophobic compounds such as hydrophobic oils can also be removed from the source zones by surfactant solutions (97). These highly hydrophobic compounds often have very low volatility, so air stripping and related technologies will not be effective at their removal from surfactant solutions. On the other hand, solvent extraction of micellar-solubilized high EACN compounds from low HLB surfactant solutions requires solvents with even higher EACN values. However, the molecular weight and viscosity of such solvents make extraction for high EACN compounds impractical (98).

To remove highly hydrophobic organic compounds from surfactant solutions, a reverse micellar extraction method relying on the solution phase behavior of low HLB surfactant systems has been proposed (98). Reverse micellar extraction is based on the principle that a Winsor Type II (water-in oil) microemulsion will form when a low HLB surfactant system is in contact with much less hydrophobic (compared to the solubilized organic compound) solvents (e.g., short-chain alcohols), as illustrated in Fig. 4. The normal micelles break up, migrate into the solvent phase, and aggregate into reverse micelles, which contain inner cores of water encapsulated by surfactant molecules and shielded from the organic solvent (99–101). Unlike the reverse-micellar extraction commonly used for recovery of proteins and other bio-products that are highly water-soluble (100–102), the hydrophobic organic compound originally solubilized within the surfactant micelles is extracted directly into the solvent phase rather than into reverse micelle cores (98). This process is promoted by both the depletion of normal micelles and

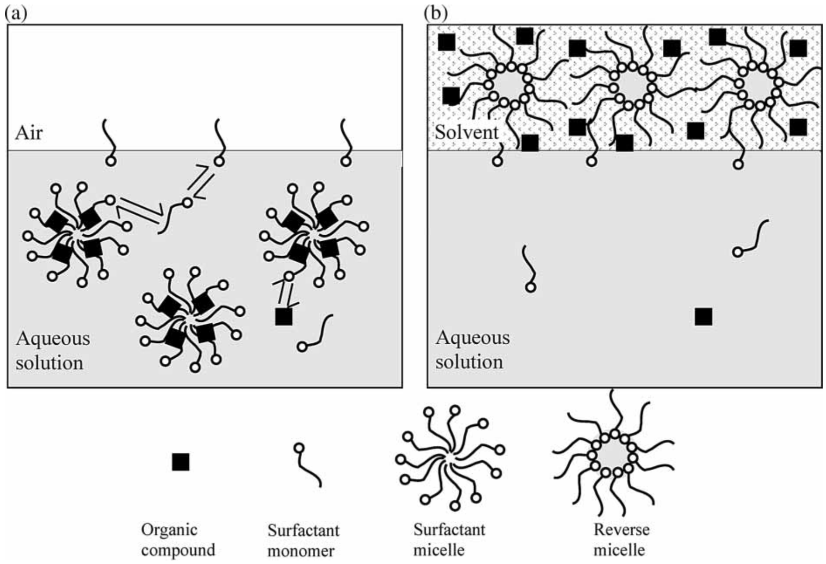

Figure 4. Schematic illustration of reverse micellar extraction: distribution of surfactant and organic compound molecules (a) before and (b) after addition of a short-chain alcohol as the extraction solvent.

the higher affinity (compared to water) of the solvent for the organic compound. The aqueous solution is essentially decontaminated after such extraction, and separation of the low-volatility organic compound and surfactant from the solvent phase may be accomplished by decreased pressure distillation (98).

Shifting of Microemulsion from Winsor Type III to Type I with Electrolyte Exchange

Although organic contaminant removal from the subsurface is highly efficient using the mobilization mechanism (25) and thus the pore volumes of flushing is reduced, contaminant separation and surfactant reuse can still be utilized for reducing the cost of surfactant and waste disposal. As shown in Fig. 1, transition of microemulsion systems from Winsor Type III to Type I can be accomplished by increasing the surfactant system HLB through adjusting the appropriate parameters. Similarly, by decreasing the surfactant solution HLB, the middle phase microemulsion will reappear. Surfactant system HLB can be adjusted by adding electrolytes and organic additives to optimize microemulsion formation through lipophilic interactions (3, 7, 12, 18, 103–105). These inorganic and organic additives can also reduce the surfactant content for a given solution phase.

Because of the important role played by electrolytes and organic additives in formulating microemulsions, it is possible to adjust the surfactant solution phase behavior by manipulating the electrolytes and organic additives in the surfactant systems. Polyvalent cations, Al^{3+} and Ca^{2+}, have much higher surface charge densities than a monovalent cation like Na^{+}, and are thus much more effective at decreasing the surfactant system's HLB. Calcium salt has been successfully applied in surfactant formulations in both laboratory (12) and field studies (106, 107) for NAPL remediation. Aluminum salt can also be potentially used in surfactant system formulation for SEAR, although there are some application concerns (108). Even though the equivalent surfactant counterion concentration remains the same after precipitating the polyvalent cations as hydroxide or carbonate by adding a base or carbonate salt of a monovalent cation (e.g., Na^{+}), a shift in the microemulsion phase behavior towards Winsor type I can occur. Laboratory experiments showed that after exchanging the polyvalent cations (Al^{3+} and Ca^{2+}) with equivalent amounts of a monovalent cation (Na^{+}), middle phase microemulsions were broken with most of the organic compounds solubilized in the middle phase separated as a free phase (11). The phase transition between Winsor Type III and Type I systems were also reversible with re-dissolution of the polyvalent cations by adding a mineral acid (HCl), which allows potential reuse of the surfactant solutions (11). On the other hand, attempts to transform the organic additive oleic acid in middle phase microemulsion systems by adding a base had no significant effect on the phase behavior, probably because oleic acid molecules in Winsor Type III microemulsion were not accessible by OH^{-}, which resided in the aqueous phase (11).

CONCLUSIONS

Surfactant enhanced solubilization of organic compound is important in numerous environmental and industrial applications. Separation of the emulsified organic compounds from surfactant streams and reuse of the surfactants can improve process economics. Waste disposal also requires the removal of both surfactants and the organic compounds from the contaminated surfactant streams. Separation processes based on inter-phase mass transfer have been developed and successfully implemented. While other separation methods based on surfactant micelle removal and surfactant solution phase behavior (Table 1) have also been developed in laboratory studies, further research is required to demonstrate their field performance and to improve their operational feasibility. Despite the significant advances made in the last two decades on separation from surfactant solutions, two major issues still need further investigation:

1. Separation of nonvolatile, hydrophobic organic compounds from low HLB surfactant systems is challenging. These nonvolatile compounds

are not amenable to air stripping. Solvent extraction is limited by the availability of hydrophobic solvents that will not be emulsified by the surfactant systems. It is also complicated by solubilization of extraction solvent into micelles, which increases the affinity of the micellar phase for organic compound and reduces extraction efficiency (26). Reverse micellar extraction can remove both the surfactant and organic compound from the micellar solution, but further separation of the nonvolatile organic compound from the surfactant is difficult.

2. Separation of semi-volatile and non-volatile organic compounds from nonionic surfactant solutions is more difficult compared to ionic surfactant systems. Nonionic surfactants become water soluble by the hydration of the ether oxygen of the polyoxyethylene group. Instead of the Krafft temperature, nonionic surfactants have cloud temperatures above which they separate into a coacervate phase. While this has led to the development of the cloud point extraction process (36, 42), both the surfactants and organic contaminants separate into the coacervate phase, thus not allowing separation of the contaminants from the surfactants. Separation of nonvolatile organic compounds from nonionic surfactant solutions may be achieved by solvent extraction, but significant partitioning of the nonionic surfactants into the extraction solvent may occur. The relatively hydrophobic behavior of nonionic surfactants makes separation of hydrophobic solutes for their solutions much more difficult compared to the case of ionic surfactants.

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