**ADVANCED MATERIALS**

Properties and Applications of Microemulsions

By *John Klier,* Christopher J. Tucker, Thomas H. Kalantar*, and *D. P. (Patrick) Green*

Microemulsions are thermodynamically stable, fluid, optically clear dispersions of two immiscible liquids. Recent interest in microemulsion systems has resulted from their utility in a broad range of applications including enhanced oil recovery, consumer and pharmaceutical formulations, nanoparticle synthesis, and chemical reaction media. However, the high levels typically required to ensure complete microemulsification and formulation stability often result in unacceptably high residue, contaminant levels, and formulation cost. One way to reduce surfactant requirements in microemulsion systems is through the use of efficient surfactants and interfacially active cosurfactants. We have explored and developed microemulsion systems based on efficient anionic surfactants and glycol ether cosurfactants that are stable to temperature and compositional changes and yet employ low levels of non-volatile surfactants. These microemulsion systems are finding utility in a range of applications, including consumer and industrial cleaning formulations, chemical reaction media, polymerization, and active ingredient delivery.
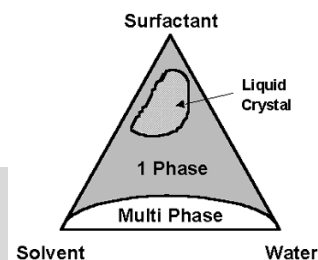
1. Introduction

Microemulsions are thermodynamically stable, fluid, optically clear dispersions of two immiscible liquids such as oil and water. Microemulsions form when a surfactant, or more commonly a mixture of surfactants and cosurfactants, lowers the oil/water interfacial tension to ultra-low values (often less than 0.001 dynes/cm), allowing thermal motions to spontaneous disperse the two immiscible phases[1] (Fig. 1). Unlike conventional emulsions, however, microemulsion domains fluctuate in size and shape and undergo spontaneous coalescence and breakup.[2]

They can exhibit water-continuous and bicontinuous structures, with typical equilibrium domain ("sub-phase") sizes ranging from 100 to 1000 Å.[1] Low surfactant concentrations produce microemulsions in equilibrium with excess dispersed phases, as shown in Figure 2, while higher surfactant concentrations can microemulsify all of the dispersed phase. As a result, microemulsion systems may be represented as surfactant/oil/water mixtures, as depicted in the pseudo-ternary phase diagram[3] of Figure 2.
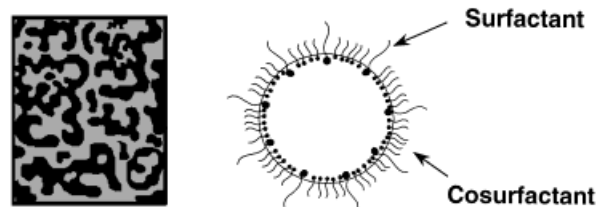

Fig. 1. Representation of a microemulsions showing (left) fluctuating domains of oil and water and (right) surfactant and cosurfactant molecules adsorbed at the oil/water interface.
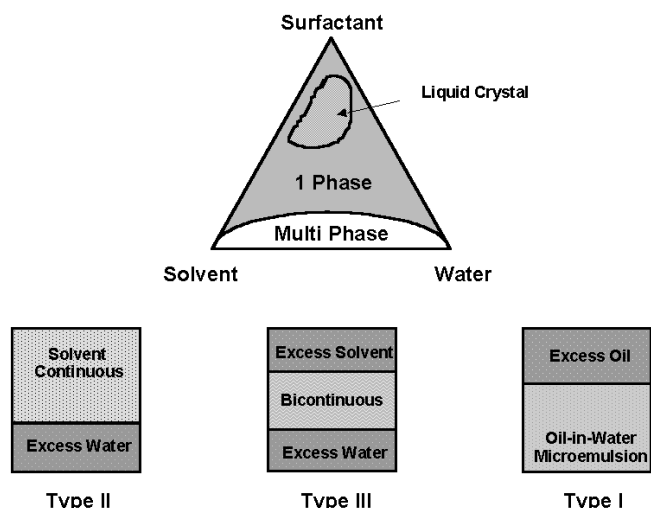

Fig. 2. Hypothetical pseudo-ternary phase diagram (fixed cosurfactant concentration) showing multiphase system at low concentrations (white), single-phase microemulsion (gray), and liquid-crystal region at high surfactant concentrations (mottled).

[*]   J. Klier
        The Dow Chemical Company
        200 Larkin, Midland, MI 48674 (USA)
        E-mail: jklier@dow.com
        C. J. Tucker, T. H. Kalantar, D. P. Green
        The Dow Chemical Company
        1712 Building
        Midland, MI 48674 (USA)

Microemulsions systems have been investigated for a broad range of technological applications. Some of the earliest detailed experimental and theoretical work was motivated by enhanced oil recovery applications involving solubilization or mobilization of oil from underground reservoirs.[4] More recently, this same approach has been directed toward oil removal from contaminated groundwater sites.[5] Microemulsions have also found broad applicability in formulated products that include oily and aqueous components. These include consumer and industrial cleaning formulations,[6,7] pharmaceutical formulations for improved drug solubilization,[8] coating formulations,[9] and many others. Most recently, microemulsions have found utility as templates for the synthesis of polymer dispersions[10] and nanoparticles[11] for a broad range of technological applications.

However, technologically useful microemulsions[12] often require high surfactant levels in order to provide sufficient interfacial coverage to completely microemulsify the required levels of ingredients, as well as to provide sufficient formulation stability to temperature and compositional changes to meet practical storage and use requirements. However, high surfactant levels are often not acceptable for economic or performance reasons. For example, high surfactant levels in consumer product formulations may leave unacceptable residues on substrates. In chemical reaction media, high surfactant levels may constitute contaminants that need to be removed, resulting in unacceptable process costs.

Our work has been focused on developing stable microemulsion systems with low levels of non-volatile surfactants for use in several application areas. Our approach has been to employ commercially available, volatile, "weak amphiphiles" such as glycol ethers in combination with small levels of "strong amphiphiles", such as high molecular weight anionic surfactants, typically with more than 22 carbons in the hydrophobic tail section. The resulting microemulsion systems typically contain water (containing less than 0.5 % dissolved electrolyte), a hydrocarbon solvent, a glycol ether cosurfactant, and a high molecular weight anionic surfactant. This approach allows extension of microemulsion technology to applications requiring or benefiting from low non-volatile surfactant levels.

2. Microemulsion Structure and Properties

2.1. Factors Influencing Microemulsion Structure and Surfactant Efficiency

As discussed above, microemulsion domain structures are often characterized as water-continuous, oil-continuous, or bicontinuous. These structures are influenced both by the water to oil ratio and by the "preferred curvature" of the surfactant, which results from the interactions of the surfactant layer with the oil and water phases.[1] For example, increasing the net affinity of the oil phase for the surfactant tail or the repulsion of surfactant tail groups from each other drives the microemulsion into a more "oil continuous" structure,[13] while increasing the size of a non-ionic surfactant's headgroup drives the microemulsion into a more "water continuous" structure.

In addition to these average curvature effects, most thermodynamic descriptions recognize that the surfactant interfacial layers in microemulsions resist "bending" in a way that increases with the extent of deformation. Without this contribution, thermal fluctuations would convolute the microemulsion interface in an unrestricted manner, leading to ever smaller microemulsion domains instead of an equilibrium domain size.[14]

A variety of thermodynamic models qualitatively capture these central equilibrium features of microemulsion behavior. These range from phenomenological models, which treat the oil/water interface as a fluctuating membrane separating oil and water phases, to lattice models, which take into account discrete surfactants at oil/water interfaces.[15,16] Many of these models describe surfactants in terms of their "amphiphile strength", a measure of the relative affinity of the surfactant molecule for residing at an oil/water interface versus partitioning into either the oil or water phase. Interfacially active molecules with low amphiphile strength include common oxygenated solvents such as glycol ethers, while conventional surfactants such as alkyl benzene sulfonates are characterized as having high amphiphile strength.[13,17]

John Klier received his Ph.D. in Chemical Engineering from Purdue University in 1989. He has been with Dow in Midland, MI since then. Currently he is Senior R&D Leader in New Businesses with responsible for initiation and implementation of cross-business research programs. Previously he worked in the Interfacial Science Discipline of Corporate R&D where he was responsible for initiating, conducting, and leading research and development efforts in the areas of colloids, functional polymers, emulsions, microemulsions, polymer dispersions, coatings, formulations, and surface treatments. John is the author of over 30 refereed journal publications and 10 patents in the areas of colloid and polymer science. He is also an Adjunct Associate Professor of Chemical Engineering at Michigan State University.

2.2. Characterization of Surfactant Efficiency

The volume of microemulsion generated per weight of surfactant added to an oil/water mixture is commonly described as the surfactant "efficiency". Surfactant efficiency can be influenced by surfactant type, molecular weight, temperature, and a host of formulation variables.[1]

In order to avoid superimposing the effects of domain curvature on efficiency measurements, surfactant efficiencies are typically determined at zero interfacial curvature (in the bicontinuous microemulsion state) at equal oil to water volumes. This characterization is typically accomplished using a "fish" diagram, shown in Figure 3.[13,18] Here, all formulation parameters except surfactant concentration and solvent
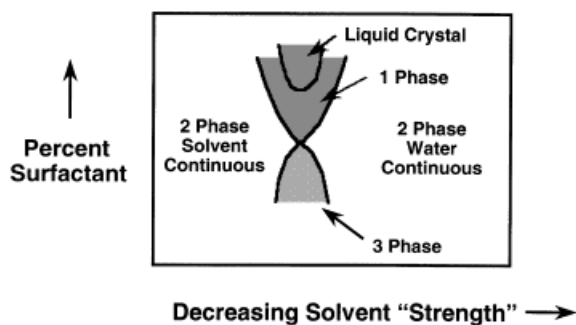

Fig. 3. "Fish" diagram used for determining surfactant efficiency. Increasing surfactant concentration results in growth of the microemulsion phase until a single-phase microemulsion system is attained. Further increases in surfactant concentration result in formation of liquid crystals. One to one oil to water ratios (by volume) are employed in the construction of these diagrams.

molecular weight (surfactant type, electrolyte content, etc.) are fixed. Increasing the solvent molecular weight reduces the solvent/surfactant interaction parameter and perturbs the microemulsion curvature from solvent-continuous to water-continuous, facilitating identification of the bicontinuous regime. Increasing the surfactant level then allows identification of the minimal amount of surfactant required to form a single-phase microemulsion (which occurs in the bicontinuous), and provides a measure of the surfactant efficiency.

2.3. Effect of Formulation Parameters on Surfactant Efficiency

Several factors, including surfactant type, electrolyte, and cosurfactant type and their concentrations, influence the surfactant efficiency. The effects of these variables were elucidated through investigation of model microemulsion systems based on an efficient anionic surfactant, purified C20–24 linear mono alkyl benzene sulfonate (ABS). This surfactant was synthesized by chlorosulfonic acid sulfonation of a distilled commercial alkyl benzene, AL-304 (Chevron, Houston, TX) and purified by extraction to contain less than 200 ppm electrolyte.[19] Gas chromatography revealed that the precursor alkyl benzene consisted of a mixture of 74 % C20, 22 % C22, and 4 % C24 tail lengths.[19] The microemulsion phase behav-

ior was determined by equilibrating the microemulsions for at least 1 week at 20.5 °C, and experimental measurements were conducted at the same temperature.

Figures 4 and 5 illustrate the effects of changing electrolyte (NaCl) concentration and cosurfactant choice on phase
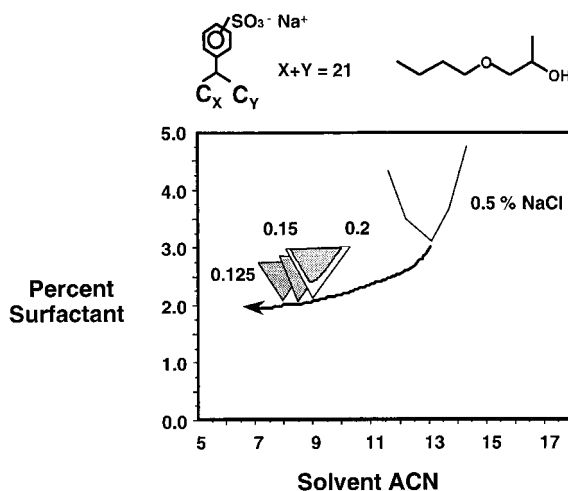

Fig. 4. Fish diagrams (top portion only) of model microemulsion systems made using 10 % PnB cosurfactant, versus electrolyte content. Liquid crystals are found in the gray areas. Numbers on chart represent wt.-% NaCl in the aqueous phase.
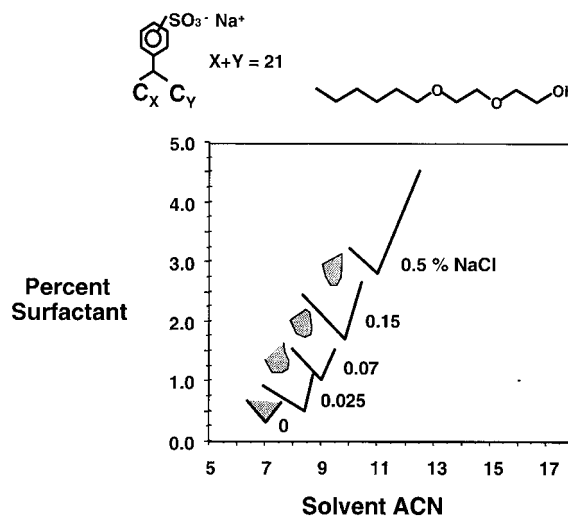

Fig. 5. Fish diagrams (top portion only) of model microemulsion systems made using 10 % C6E2 cosurfactant, versus electrolyte content. Numbers on chart represent wt.-% NaCl in the aqueous phase.

behavior and surfactant efficiency of these model microemulsions. For illustration, two commercially available cosurfactants, propylene glycol butyl ether (PnB) and diethylene glycol hexyl ether (C6E2), with widely differing interfacial activities were chosen. As shown in Figures 4 and 5, reducing electrolyte concentrations requires a compensating reduction in solvent molecular weight (alkane carbon number or "ACN") to maintain a bicontinuous microemulsion structure. Lower electrolyte concentrations also lead to reduced surfactant levels required to form single-phase microemulsions. The

magnitude of this effect is strongly influenced by the cosurfactant selection as shown by comparing Figures 4 and 5. Here the microemulsions formulated with the more amphipathic cosurfactant, diethylene glycol monohexyl ether, require significantly less surfactant than those formulated with propylene glycol monobutyl ether.

These effects were explored in more detail by analyzing the compositions and domain sizes of microemulsion middle phases in the three-phase bicontinuous microemulsion regimes found below the single-phase regions depicted in Figures 4 and 5. Here 1 % surfactant concentrations and 10 % cosurfactant concentrations (weight in grams to total microemulsion volume in milliliters) and a 1:1 oil/water ratio (volume/volume) were employed. Gas chromatography was used to estimate the microemulsion compositions, while small angle X-ray scattering (SAXS) was used to estimate the average domain size.[20]

Figure 6 reveals that reducing the electrolyte concentration in these three-phase systems leads to a dramatic increase in
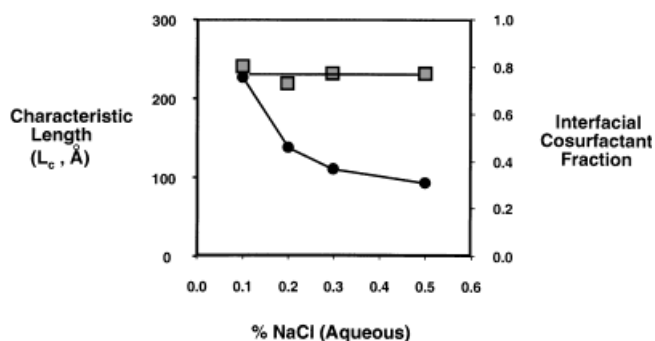

Fig. 6. Characteristic lengths (circles) and percent of total cosurfactant residing at the oil/water interface (squares), in three-phase microemulsion systems showing that changing aqueous phase electrolyte concentrations leads to large changes in microemulsion domain size (characteristic length) but does not affect the interfacial composition. Here all detectable ABS surfactant resides at the oil/water interface. Surfactant concentration was 1 % and cosurfactant concentration was 10 % (weight to total volume of microemulsion).

the average microemulsion domain size (characteristic length) without changing the interfacial composition (as a percentage of the total available cosurfactant). Similar effects were observed for both PnB and C6E2 cosurfactants.

Here, the apparent cosurfactant molecular areas, *a*, (calculated from domain sizes (determined by SAXS) and compositional data using the relationship $a = 6\phi_1\phi_2/C_s d$, where *d* is the domain size, ϕ_1 and ϕ_2 are the volume fractions of the oil and water subphases, respectively, C_s is the amphiphile concentration at the interface, and *a* is the area per surfactant molecule[21]), remained approximately constant at 30 Å^2/molecule and did not change with electrolyte or surfactant concentration. Therefore, changes in surfactant efficiency resulting from changing electrolyte or surfactant concentration were attributed primarily to changes in the convolution (or "crumpling") of the interface and not to molecular area changes. At very low electrolyte concentrations, the interface stiffens to such an extent, however, that lamellar liquid crystals form and surfactant efficiency reaches a plateau. A cartoon of this effect is

shown in Figure 7. This behavior was attributed to an increase in surfactant–surfactant repulsion arising from simultaneous
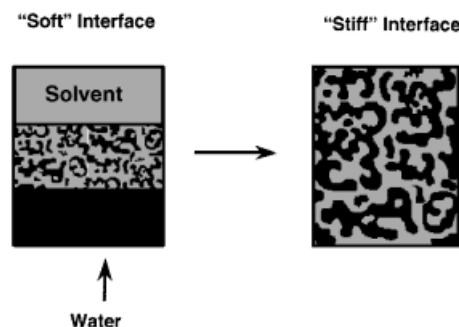

Fig. 7. Cartoon of microemulsion domains expanding ("uncrumpling") with reduced electrolyte concentration.

reduction of electrostatic screening and increased surfactant tail solvation upon reducing electrolyte concentration and solvent molecular weight.

The higher surfactant efficiencies obtained with C6E2 versus PnB may be explained by the higher C6E2 concentration residing at the oil/water interface (Fig. 8). As a result, the C6E2 cosurfactant covers a larger proportion of the oil/water
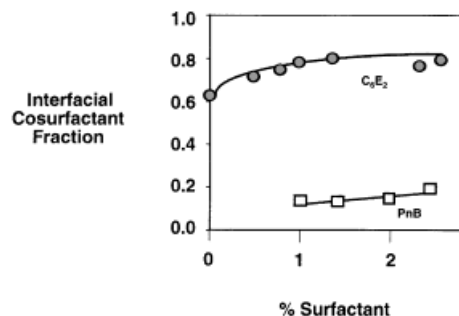

Fig. 8. Relative concentrations of PnB and C6E2 (as a fraction of their total content in the system) at the interface in three-phase microemulsion systems versus ABS surfactant content at 0.5 % NaCl electrolyte in aqueous phase.

interface, allowing use of lower ABS concentrations to produce microemulsions with a given oil and water volume. Interestingly, in the C6E2-containing formulations, the ABS surfactant acts as a "dopant". It occupies a minor proportion of the interface (as low as 1 % of the interfacial area in some cases), but nevertheless has a large effect on domain size and, therefore, overall microemulsification capacity and efficiency.

2.4. Effect of Molecular Parameters on Surfactant Efficiency

While formulation parameters such as electrolyte content and cosurfactant choice can have a dramatic effect on surfactant efficiency, surfactant architecture can also have a profound influence on efficiency, as shown in Figure 9. Here, microemulsions were formulated using two pure surfactants, a 2-position C18 alkyl benzene sulfonate (prepared via alkylation using a shape-selective zeolite, followed by sulfonation) and an 8-position alkyl benzene sulfonate (prepared by a
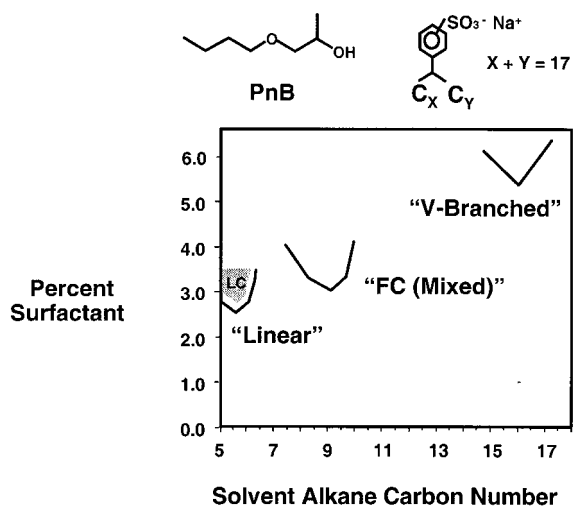
Fig. 9. Fish diagrams showing effect of surfactant branching in model microemulsions with PnB cosurfactant.

Grignard reaction followed by alkylation). These were contrasted with microemulsions prepared using a "mixed" surfactant synthesized via Friedel Crafts alkylation.

Clearly, the branched surfactant has a much lower efficiency than the more linear surfactant at this "high" electrolyte concentration (0.5 wt.-% NaCl). This behavior can be explained by the propensity of the branched surfactant to produce microemulsions that are relatively more "crumpled", resulting in smaller domain sizes and increased surfactant requirement per microemulsion volume. This behavior may be due to an increased susceptibility to electrostatic screening via added electrolyte that can result from higher intersurfactant spacing arising from the branched tail architecture. This model is supported by the similar efficiencies of the linear and branched surfactants at low electrolyte concentrations. Comparison of several anionic and nonionic surfactants under a single set of formulation conditions (Fig. 10), follows the expected trends with branched non-ionic (excluded volume headgroup repulsions only) showing the lowest efficiency and high molecular weight
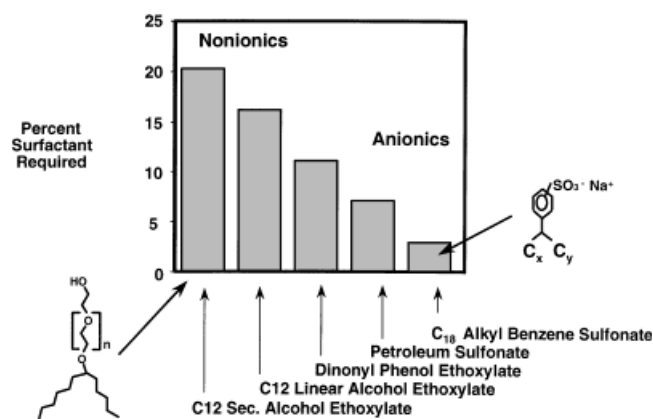

Fig. 10. Efficiencies of several surfactants in microemulsions formulated using a PEB cosurfactant (Propoxyethyloxybutyl ether) and high (0.5 % NaCl) electrolyte content.

anionic (electrostatic repulsions) showing the highest efficiency.

Clearly, several important formulation and molecular variables influence the surfactant efficiency in microemulsion systems. Use of interfacially active cosurfactants allows surface coverage principally by the cosurfactant molecules, reducing the need for high molecular weight surfactants. Controlling interactions such as electrostatic repulsions between surfactant molecules can also greatly influence the surfactant efficiency by altering the size (and hence the surface to volume ratio) of the microemulsion domains. Finally, surfactant architecture can play an important role in determining microemulsion efficiency. The efficiency of branched surfactants may be highly susceptible to electrolyte content, whereas linear surfactants may show relativity little effect.

3. Applications

3.1. Formulations

Over the past several years, we have applied microemulsions to a variety of technological problems, including consumer and commercial cleaning product formulations, delivery systems, polymerization media, and chemical reaction media. Advantages of microemulsion formulations over their solvent-based counterparts include high water content resulting in low cost, reduced volatile organic content, improved formulation flexibility (ability to formulate water and solvent borne ingredients) and ability to clean both water- and oil-soluble substrates.

Figure 11 shows the compositions and some properties of model microemulsion formulations based on high molecular

Formulation	Solvent	VOC	Flash Pt.	Flame	Viscosity (cP)
A	heptane	45 %	27 F	Low	6
B	limonene	45 %	123 F	No	7.5
C	naptha	45 %	145 F	No	7.5

4 % Anionic Surfactant
15 % Volatile Cosurfactant Blend
30 % Hydrocarbon Solvent
51 % Water

Fig. 11. Chart of three representative concentrated, glycol-ether-based microemulsion systems useful for formulating specialized microemulsion compositions and their properties.

weight anionic surfactants, glycol ether cosurfactants, and common hydrocarbon organic solvents. These microemulsions are useful as high-performance industrial cleaners alone and can be further formulated to create specialized high-performance, low surfactant microemulsions for a variety of industrial and consumer applications.

Temperature and additive stability are important considerations in creating a useful microemulsion. Through the judicious use of glycol ether/anionic surfactant blends, we pre-

pared microemulsion systems with both broad temperature and formulation stability as shown in Figure 12. We believe that this temperature stability is due to the compensating effects of the anionic surfactant and glycol ether cosurfactant
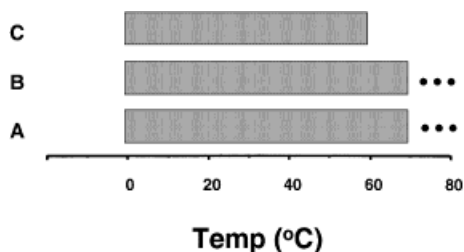

Fig. 12. Diagram showing broad temperature stability of the microemulsion systems in Figure 11.

with regard to preferred interfacial curvature. Typically, microemulsions with high proportions of anionic surfactants become more water-continuous with increasing temperatures, while microemulsions containing high proportions of glycol ether cosurfactant become more solvent-continuous due to ether hydrophobic interactions. A balance of these two components, in practice, give rise to a broad temperature stability range.

Furthermore, the structure of the microemulsion formulations can have a significant effect on their cleaning performance. Figure 13 shows the cleaning of a model oily soil, petroleum jelly, by a model microemulsion composition, where
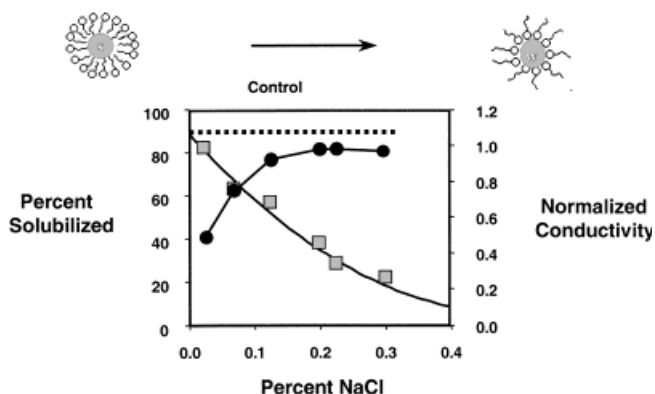

Fig. 13. Diagram showing cleaning of petroleum jelly versus microemulsion structure for microemulsions containing 50 % water. Adding electrolyte drives microemulsions from water-continuous toward solvent-continuous (low conductivity), and improves cleaning performance to a value similar to that of the water-free control.

the microemulsion structure has been perturbed from water-continuous to solvent-continuous via electrolyte addition. Clearly, the solvent-continuous structures show a higher rate of oily soil cleaning than the water-continuous structures, and this effect can be attributed to the higher solvent diffusivity in these systems,[19] leading to faster delivery of the solvent to the soil substrate. Therefore, microemulsion systems may be optimized for oily soil cleaning via manipulation of formulation variables to produce solvent-continuous systems.

Practical examples of microemulsion formulations employed in the preparation of fabric pretreaters can be found in

the literature.[12,22] Klier et al.,[12] for example, showed low viscosity (22 centistokes) single-phase oil-continuous microemulsions containing 50 wt.-% water can be made with only 5 % sodium C20–24 alkyl toluene sulfonate surfactant, (18 % dipropylene glycol *n*-butyl ether cosurfactant and 27 % C13 hydrocarbon). These oil-continuous microemulsions are useful as cleaners for oily soils and stains. In contrast, attempts to make similar microemulsions using low molecular weight anionic surfactants such as sodium lauryl sulfate, generally result in two-phase systems (unless very high surfactant concentrations are used), due to the poor efficiency of this anionic surfactant. Similarly, in the literature[22] it is shown that liquid microemulsions at elevated temperatures are quenched into kinetically stable solid or gel formulations containing high water contents. The microemulsion approach facilitates coupling of high levels of water with organic solvent and also facilitates processing.

3.2. Chemical Reaction Media

Chemical reactions such as oxidation, hypochlorination, nitration, enzymatic reactions, and many others involve multiphase reactions where an aqueous reactant reacts with oily substrates. For example, hypochlorination reactions of water-insoluble liquid reactants produce industrially useful chlorohydrins and their derivatives (epoxides and epoxide derivatives). However, these reactions have been difficult to carry out at high yield due to side reactions that occur within the excess oil phase to form dichlorides and bis ethers, as depicted in Figure 14. Increasing the interfacial area between the organic and aqueous phases is expected to increase the chlorohydrin yield.
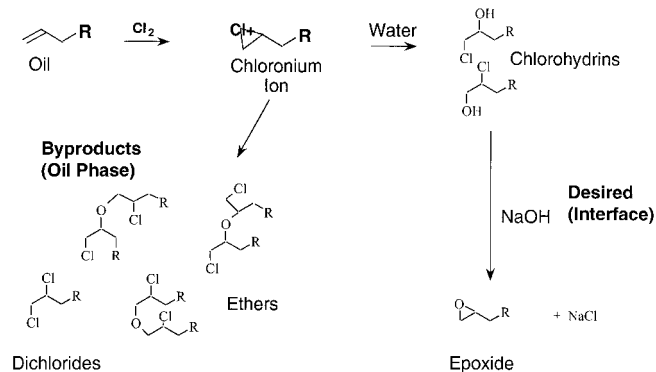

Fig. 14. Hypochlorination chemistry showing desired and undesired reaction products.

Indeed, when the organic substrates and products in these reactions were microemulsified using a surfactant, the yields shifted dramatically to the desired chlorohydrins.[23] For example, Figure 15 shows the yield of a hexene hypochlorination reaction conducted under batch conditions with increasing surfactant concentrations. The reaction was run by placing 1 L of water containing the surfactant in the reactor, to which was added 20 g (0.23 mol) hexene and 0.23 mol chlorine con-
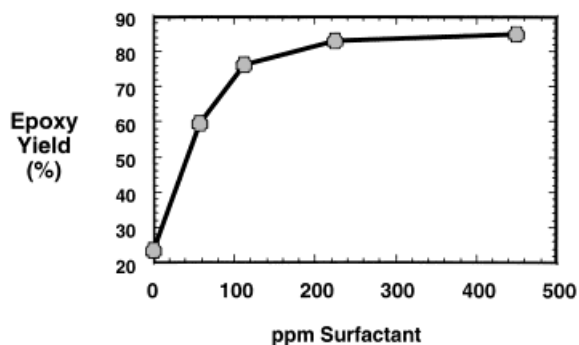
Fig. 15. Hypochlorination yield versus surfactant concentration.

tinuously over 15 min at 1000 rpm agitation. The effects of microemulsion phase behavior on the epoxide yield in multi-phase microemulsion systems are further illustrated in Figure 16 (fixed surfactant concentration, 112 ppm of model alkyl sulfonate surfactants under similar conditions). Chang-
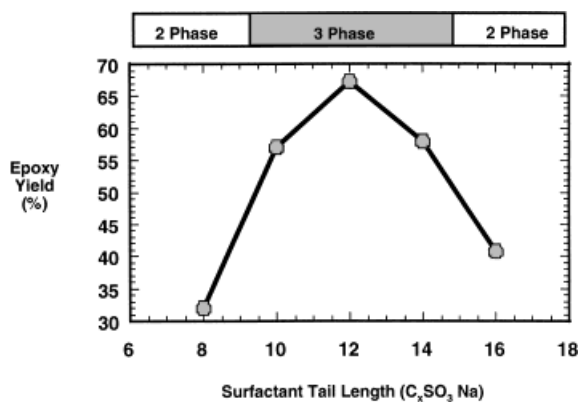

Fig. 16. Hypochlorination yield versus microemulsion phase behavior.

ing the surfactant tail length perturbed the microemulsion system from water-continuous to solvent-continuous, and the highest epoxide yield corresponds to the formation of a three-phase microemulsion, which is known to produce ultra-low oil/water interfacial tension. These data suggest that formation of these three-phase systems facilitates rapid and intimate mixing of the oil and water phases and promotes the interfacial reactions that favor chlorohydrin formation.

It should also be noted that the chlorohydrins were effective cosurfactants, making the addition of extraneous cosurfactant unnecessary. By employing a surfactant that functions in conjunction with the indigenous cosurfactant, very low surfactant additive levels were employed (such as in the example above).

4. Summary

Robust microemulsions with low surfactant levels can be formulated via the use of efficient surfactants, interfacially active cosurfactants, and proper formulation conditions (e.g., low electrolyte content). Microemulsions formulated according to these strategies have advantages of very high microemulsification capacity, low surfactant residue, and low cost. This approach has been used to reduce the cost and improve the performance of several consumer product formulations. Similarly, interfacial chemical reactions can be facilitated using microemulsion-forming surfactants, in combination with indigenous cosurfactants. This strategy has been used to identify improved, simple, novel routes to industrially useful materials such as chlorohydrins and epoxides.

[1] J. Biais, B. Clin, P. Laolanne, in *Microemulsions: Structure and Dynamics* (Eds: S. E. Friberg, P. Bothorel), CRC Press, Boca Raton, FL **1987**, Ch. 1.
[2] R. Zana, J. Lang, in *Microemulsions: Structure and Dynamics* (Eds: S. E. Friberg, P. Bothorel), CRC Press, Boca Raton, FL **1987**, Ch. 6.
[3] M. Penders, R. Strey, *J. Phys. Chem.* **1995**, *99*, 10 313.
[4] M. Schwuger, K. Stickdorn, *Chem. Rev.* **1995**, *95*, 849.
[5] C. C. West, J. H. Harwell, *Environ. Sci. Technol.* **1992**, *26*, 2324.
[6] F. Schambil, M. Schwuger, *J. Colloid Polym. Sci.* **1987**, *265*, 1009.
[7] J. Mihelic, L. B. Luttinger, *US Patent 5 401 326*, **1995**.
[8] M. J. Lawrence, *Eur. J. Drug Metabolism Pharmakokinetics* **1994**, *3*, 257.
[9] H. B. Dawson, J. J. Czipri, *Wood Protection* **1991**, *1*, 55.
[10] W. F. C. Sager, *Curr. Opin. Colloid Interface Sci.* **1998**, *3*, 276.
[11] I. Capek, *Adv. Colloid Interface Sci.* **1991**, *80*, 85.
[12] J. Klier, G. M. Strandburg, C. J. Tucker, *US Patent 5 597 792*, **1997**.
[13] M. Bourrel, R. S. Schechter, *Microemulsions and Related Systems*, Marcel Dekker, New York **1988**.
[14] B. Widom, *J. Chem. Phys.* **1984**, *81*, 1030.
[15] S. A. Safran, T. Tlusty, *Ber. Bunsenges. Phys. Chem.* **1996**, *100*, 252.
[16] M. Laradji, H. Guo, M. Grand, M. J. Zuckermann, in *Advances in Chemical Physics LXXXIX* (Eds: I. Prigogine, S. A. Rice), Wiley, New York **1995**, p. 159.
[17] K. V. Schubert, R. Strey, S. R. Kline, E. W. Kaler, *J. Chem. Phys.* **1994**, *101*, 5343.
[18] M. Kahlweit, R. Strey, D. Haase, H. Kunieda, T. Schmeling, B. Faulhaber, M. Borkovec, H. F. Eicke, G. Busse, F. Eggers, T. Funck, H. Richmann, L. Magid, O. Soderman, P. Stilbs, J. Winkler, A. Dittrich, W. Jahn, *J. Colloid Interface Sci.* **1987**, *118*, 436.
[19] J. Klier, R. Suarez, D. P. Green, A. M. Kumar, C. J. Tucker, B. Landes, D. Redwine, *J. Am. Oil Chem. Soc.* **1997**, *74*, 861.
[20] L. Auvray, in *Micelles, Membranes, Microemulsions and Monolayers* (Eds: W. M. Gelbart, A. Ben-Shaul, D. Roux), Springer, New York **1994**, Ch. 7.
[21] H. Kellay, B. P. Binks, Y. Hendrikx, L. T. Lee, J. Meunier, *Adv. Colloid Interface Sci.* **1994**, *49*, 85.
[22] J. Klier, G. M. Strandburg, C. J. Tucker, *US Patent 5 538 662*, **1996**.
[23] D. P. Green, J. Klier, C. J. Tucker, M. S. Ferritto, *US Patent 6 051 742*, **2000**.