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Organic Reactions in Microemulsions

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Microemulsions, i.e., thermodynamically stable, one-phase mixtures of oil, water and surfactants, are useful as reaction media as a way to overcome the reactant incompatibility problem that one frequently encounters in organic synthesis. The use of a microemulsion can be seen as an alternative to phase-transfer catalysis, i.e., use of a two-phase system with added phase-transfer agent. The microemulsion approach and phase-transfer catalysis can also be combined, i.e., the reaction can be performed in a microemulsion in the presence of a small amount of a phase-transfer agent. A very high reaction rate may then be obtained. The reaction rate in a microemulsion is often influenced by the charge at the interface and this charge depends on the surfactant used. For instance, reactions involving negatively charged species will be accelerated by the use of a cationic surfactant. This effect is analogous to micellar catalysis and may be termed microemulsion catalysis. The acceleration is more pronounced when the surfactant counterion is small and weakly polarizable. Microemulsions can also be used to induce regiospecificity of organic reactions. Organic molecules with one more polar and one less polar end will accumulate at the oil-water interface of microemulsions. They will orient at the interface so that the polar part of the molecule extends into the water domain and the nonpolar part extends into the hydrocarbon domain. A water-soluble reagent will react from the "water side", i.e., attack the polar part of the amphiphilic molecule, and a reagent soluble in hydrocarbon will react at the other end of the amphiphilic molecule. This review demonstrates that microemulsions can be a useful for (i) overcoming reactant incompatibility, (ii) speeding up reactions of one polar and one apolar reactant (microemulsion catalysis), and (iii) inducing regiospecificity.
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1. Introduction

Reagent incompatibility is a frequently encountered problem in preparative organic chemistry. It may occur when a lipophilic organic compound soluble in hydrophobic media but insoluble in water and other polar solvents is allowed to react with a very hydrophilic organic substance or with an inorganic salt that is insoluble in most organic solvents. Well-known examples are alkaline hydrolysis of lipophilic esters, oxidative cleavage of olefins with permanganate-periodate, addition of hydrogen sulfite to aldehydes and to terminal olefins, preparation of alkyl sulfonates by treatment of an alkyl chloride by sodium sulfite or by addition of sodium hydrogen sulfite to an epoxide. The list can be extended further. In all examples given there is a compatibility problem to be solved if the organic component is a large apolar molecule.

There are different ways to solve the problem of incompatibility between the reacting species. An obvious approach is to find a solvent or a solvent combination capable of dissolving both the lipophilic and the hydrophilic species. Polar, aprotic solvents are sometimes useful for this purpose but many of these are unsuitable for large scale work due to toxicity, high cost, and problems in removing them by low-vacuum evaporation.

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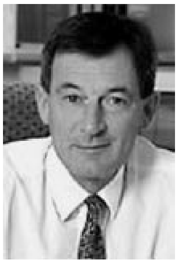


Krister Holmberg received his Ph.D. in Organic Chemistry in 1974 from Chalmers University of Technology. After working as a research scientist first in the pharmaceutical industry, then in the chemical industry, he became Research Director of Berol Kemi, nowadays Akzo Nobel Surfactants, in 1988. In 1991 he became Director of the Institute for Surface Chemistry in Stockholm, Sweden and in 1998 he was appointed Professor of Surface Chemistry at Chalmers University of Technology. In 2003 he became Head of the Department of Chemical and Biological Engineering. His research interest concerns organic and bioorganic reactions in microheterogeneous media, synthesis and characterization of novel surfactants, and preparation of nanomaterials using self-assembled surfactants as template. He has published more than 200 scientific papers, written or edited six books and he is the inventor or coinventor of 35 patents. He is currently the supervisor of eight Ph. D. students at Chalmers University of Technology.

Alternatively, the reaction may be carried out in a mixture of two immiscible solvents. The contact area between the phases may be increased by agitation. Phase-transfer reagents, in particular quaternary ammonium compounds, are useful aids in many two-phase reactions. Also crown ethers are very effective in overcoming phase contact problems; however, their usefulness is limited due to their high price. (Open-chain polyoxyethylene compounds often give a "crown ether effect" and may constitute a practically interesting alternative as phase-transfer reagents.)

A third approach is to use a microemulsion or a related type of organized solution. Microemulsions are excellent solvents both for hydrophobic organic compounds and for inorganic salts. Being macroscopically homogeneous but microscopically dispersed, they can be regarded as something between the solvent-based one-phase systems and the true two-phase systems. The capability of microemulsions to solubilize a very broad spectrum of substances in one single formulation has found many technical applications. They are, for instance, unsurpassed for cleaning of hard surfaces – dirt is often a complex mixture of hydrophilic and hydrophobic components.

There has been considerable interest in the use of microemulsions as media for organic synthesis in recent years. Not only can such a formulation be a way to overcome compatibility problems, the capability of microemulsions to compartmentalize and concentrate reactants can also lead to considerable rate enhancement compared to one-phase systems. A third aspect of interest for preparative organic synthesis is that the large oil-water interface of the system can be used as a template to induce regioselectivity.

The three aspects of use of microemulsions for organic synthesis, overcoming reagent incompatibility, enhancing reaction rate, and inducing regioselectivity, will be discussed in this review. It will also be shown that the microemulsion approach can be combined with phase-transfer catalysis to give reaction media of high reactivity for certain nucleophilic substitution reactions.

The use of microemulsions as media for organic reactions suffers from one inherent drawback: the need to use large amounts of surfactants to produce the microemulsion. In order to obtain acceptable process economy on large-scale operations, techniques must be available for efficient removal and reuse of the surfactant. This aspect of microemulsion-based organic synthesis will also be discussed.

The topic of microemulsion-based organic synthesis has been reviewed before, see for instance ref.[1–3]. In this review emphasis will be put on the more recent development.

2. Microemulsions

Microemulsions are thermodynamically stable mixtures of oil, water and surfactant.[1,2] The oil is usually a hydrocarbon or a solution of a solute in a hydrocarbon. The surfactant may be a single amphiphilic species but it may also be a combination of two or more amphiphiles. A common practice is to use a combination of a normal surfactant and a medium chain alcohol as "surfactant" component. The medium chain alcohol is then often referred to as cosurfactant. A microemulsion is transparent or slightly opaque. It is macroscopically homogeneous (a one-phase system) but microscopically heterogeneous. It contains oil and water domains of nanometer-sized dimensions. The interface between the domains is very large and is covered by a monolayer of surfactant. The structure is highly dynamic. Each interface disintegrates and reforms in the time scale of milliseconds.

Microemulsions have much in common with micellar solutions. They are both thermodynamically stable, which means that they will remain one-phase systems for ever (provided the surfactants stay intact). They form spontaneously when the components are mixed. They are transparent, they are usually low viscous, and they are both highly dynamic systems. Microemulsions can be regarded as micellar solutions that have solubilized oil into the apolar surfactant tail region.

Emulsions are very different. They are not thermodynamically stable and considerable mechanical energy is normally needed to create them. All emulsions will eventually separate into an oil and a water phase. Some emulsions, for instance in the food area, are said to be "stable" but that does not mean that they are thermodynamically stable. It just means that the time until phase separation occurs is long. Emulsions are not dynamic systems, rather they are static. The interface in an emulsion does not constantly disintegrate and reform as it does in a microemulsion and in a micellar system. The dimensions in an emulsion is also much larger, typically in the micrometer range, which means that the oil-water interface in an emulsion is orders of magnitude smaller than in a microemulsion.

Emulsions have also been explored as media for organic synthesis but they are generally not as useful as microemulsions. This can be understood considering that

– microemulsions have a much larger interfacial area and the reaction occurs at the interface,

– the high dynamics of microemulsions is likely to favour contact between the reactants.

Emulsions consist of either oil droplets in water or water droplets in oil and the droplets are spherical unless the continuous medium has very high viscosity. An oil-in-water emulsion can undergo phase inversion to yield a water-in-oil emulsion and vice versa and spherical droplets are always formed. A microemulsion that contains substantial amounts of both oil and water may consist of oil droplets in water, water droplets in oil or be bicontinuous, i.e., consist of continuous domains of both oil and water. A microemulsion formulated with a nonionic surfactant of the fatty alcohol ethoxylate type may go from oil droplets in water via a bicontinuous structure to water droplets in oil by raising the temperature. This is illustrated in Figure 1. As can be seen, the curvature of the interface in the microemulsion proceeds from being highly curved towards oil via a zero net curvature to highly curved towards water. All structures are thermodynamically stable and the interfacial area is approximately the same regardless of the internal structure.

Also with respect to the internal structure there are clear similarities between microemulsions and micellar solutions. The aggregates in a micellar solution of the same surfactant as discussed above for the microemulsion may go from spheres at low temperature to gradually more elongated (in one or two dimensions, i.e., rod-like or disc-like) as the temperature is raised. At high temperature there may be infinitely long surfactant bilayers in water with a zero net curvature. This is the so-called sponge phase, or L3-phase, which can be said to be equivalent to the bicontinuous microemulsion in the ternary oil-water-surfactant system. Oil-in-water, bicontinuous and water-in-oil microemulsions are all useful as reaction media for organic synthesis.

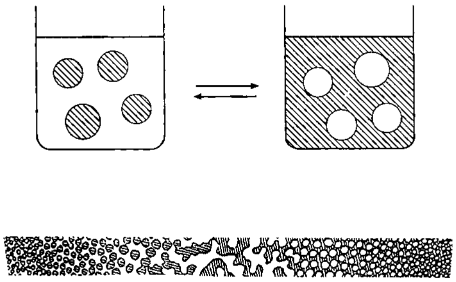


Figure 1. Internal structure of emulsions and microemulsions. Top: an emulsion showing an abrupt phase transition from oil-in-water to water-in oil. Bottom: a microemulsion showing a gradual change from water-continuous, via bicontinuous to oil-continuous.

If the amount of surfactant used in a formulation is not sufficient to make a microemulsion of the entire volume of oil and water, two- or three-phase systems may form in which a microemulsion is in equilibrium with an excess oil phase, an excess water phase or excess oil and water phases. These are referred to as Winsor I, Winsor II and Winsor III systems, respectively. Winsor systems are definitely of interest as media for organic synthesis. For the surfactant discussed in connection to Figure 1, i.e., a fatty alcohol ethoxylate, the formulation may be a Winsor I system at low temperature and proceed via a Winsor III system to a Winsor II system as the temperature is raised. This is illustrated in Figure 2. As will be discussed in the section "Work-up approaches", such phase transitions can be used to separate the product from the surfactant.

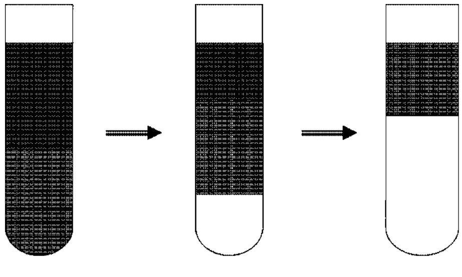
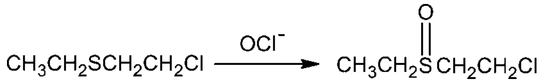


Figure 2. Left test tube: a microemulsion of oil-in-water type (bottom) in equilibrium with excess oil (Winsor I system). Middle test tube: a bicontinuous microemulsion (middle) in equilibrium with excess oil and water (Winsor III system). Right test tube: a microemulsion of water-in-oil type (top) in equilibrium with excess water (Winsor II system). The arrows show a transition from Winsor I to Winsor III and on to Winsor II, which may take place on raising the temperature when a nonionic surfactant of fatty alcohol ethoxylate type is used in the formulation.

3. Overcoming reactant incompatibility

Several studies have shown that microemulsions are suitable reaction media for organic reactions involving two reactants of widely different polarity. A properly formulated microemulsion can dissolve both reactants and the large oil-water interfacial area enables contact between the two otherwise incompatible species. It is natural to compare the microemulsion approach with phase-transfer catalysis because in both cases an auxiliary agent, a surfactant or a phase-transfer agent, is added to speed up the reaction. For some reactions the reactivity in a microemulsion is of the same order as that in a two-phase system with added phase transfer agent[3] but in other instances the reaction is considerably faster in a microemulsion.[4,5] It will be demonstrated in the section "Combining the microemulsion approach with phase-transfer catalysis" that very high reactivity can be obtained by combining the two approaches.

F. Menger was one of the pioneers in the exploration of microemulsions as media for organic reactions. In an early paper together with Elrington he demonstrated, for detoxification of mustard, how effective a properly formulated microemulsion can be in overcoming reagent incompatibility.[4] Mustard is a well-known chemical warfare agent. Although it is susceptible to rapid deactivation in laboratory experiments where rates are measured at low substrate concentrations, its destruction in practice is not easy. Due to its extremely low solubility in water, it remains for months on a water surface. Addition of strong caustic does not markedly increase the rate of reaction. Microemulsions were explored as media for oxidation of "half-mustard", $CH_3CH_2SCH_2CH_2Cl$, which was used as a model for mustard, $ClCH_2CH_2SCH_2CH_2Cl$, in order to reduce toxicity (Figure 3). Oxidation with hypochlorite turned out to be extremely rapid in both oil-in-water and water-in-oil microemulsions. In formulations based on anionic, nonionic or cationic surfactant oxidation of the half-mustard sulfide to sulfoxide was complete in less than 15 s. The same reaction took 20 min when a two-phase system, together with a phase-transfer agent, was employed.



$$CH_3CH_2SCH_2CH_2Cl \xrightarrow{OCl^-} CH_3CH_2\overset{\overset{O}{\|}}{S}CH_2CH_2Cl$$

Figure 3. Transformation of 2-chloroethyl ethyl sulfide (half-mustard) into 2-chloroethyl ethyl sulfoxide by oxidation with hypochlorite.

Menger has later revisited the reaction, now exploring the use of cryochemistry for the purpose.[6] Microemulsions that resist freezing and phase separation at –18 °C were developed using water-propylene glycol as aqueous component and fatty alcohol ethoxylates with long polyoxyethylene chains as surfactants. These microemulsions were used as media for destruction of different types of chemical warfare agents by reaction at –18 °C, either by hydrolysis or by oxidation.

The efficiency of a microemulsion as reaction medium was very pronounced in the synthesis of a surface-active product, decyl sulfonate.[3] Decyl bromide and sodium sulfite were used as starting materials and two different microemulsions were tested, one water-in-oil and one bicontinuous. The reaction was also carried out in a two-phase system with either a crown ether or a quaternary ammonium salt (Q salt) as phase-transfer agent. As can be seen from Figure 4, the reaction proceeded at a reasonable rate in the microemulsions but ceased at an early state in the two-phase systems. The poor reactivity in the latter systems was believed to be due to the phase-transfer agent partitioning entirely into the hydrocarbon phase due to ion pair formation with the lipophilic anion formed. Too strong association with a lipophilic anion will prevent the Q salt or crown ether from going back into the aqueous phase to pick up another reacting anion and transfer it into the organic phase where the reaction occurs.[3,7] This is likely to be a general phenomenon and microemulsions may, thus, constitute a particularly interesting alternative to phase-transfer catalysis in cases where the product is a lipophilic anion.

The same reaction has been investigated by other workers.[8] A double-tailed cationic surfactant, dioctyldimethylammonium chloride, was used as amphiliphile to create the microemulsion. The surfactant counterion, chloride, was claimed to substitute for bromide to give decyl chloride, which reacted further to the sulfonate. This suggested reaction path may be questioned considering that an alkyl bromide is generally more reactive than an alkyl chloride. Formation of a surface-active product of a charge opposite that of the added surfactant caused instability of the system. Two phases appeared at an early state and most of the reaction occurred in an emulsion rather than a microemulsion. In the previously mentioned work, which was performed in a system based on nonionic surfactant with only small amount of cationic surfactant added, the reaction medium remained a one-phase solution during the entire course of the reaction.[3] In more recent work reactions between sodium sulfite and different decyl halides were investigated in emulsions instead of microemulsions as reaction media. Basically the same result in terms of reactivity of the halide anions were obtained.[9]

An attempt was made to correlate the rate of hydrolysis of acetylsalicylic acid with the structure of the microemulsion used as reaction medium.[10] Water was added to the formulation and it was found that the reaction rate changed abruptly when the system passed from water-in-oil to bicontinuous and again when the bicontinuous microemulsion was transformed into an oil-in-water microemulsion. For a microemulsion based on a nonionic surfactant the bicontinuous microemulsion gave the highest reaction rate, for a microemulsion based on an anionic surfactant the oil-in-water system was the most reactive, and for a cationics-based microemulsion the water-in-oil system gave the highest reaction rate. Similar results were obtained in another study of the same reaction.[11] In previous studies of reactivity in different types of microemulsions based on nonionic surfactants, no major differences in reaction rate were observed, however.[12]

Microemulsions can be formulated with a chlorinated hydrocarbon as oil component and such microemulsions have been explored for organic synthesis. Epoxidation of olefins using a manganese catalyst was investigated in bicontinuous microemulsions based on an alkyl glucoside surfactant.[13] The reactions went well but it was found that the stereoselectivity was different in the microemulsion than in a two-phase system. This is probably related to the large internal

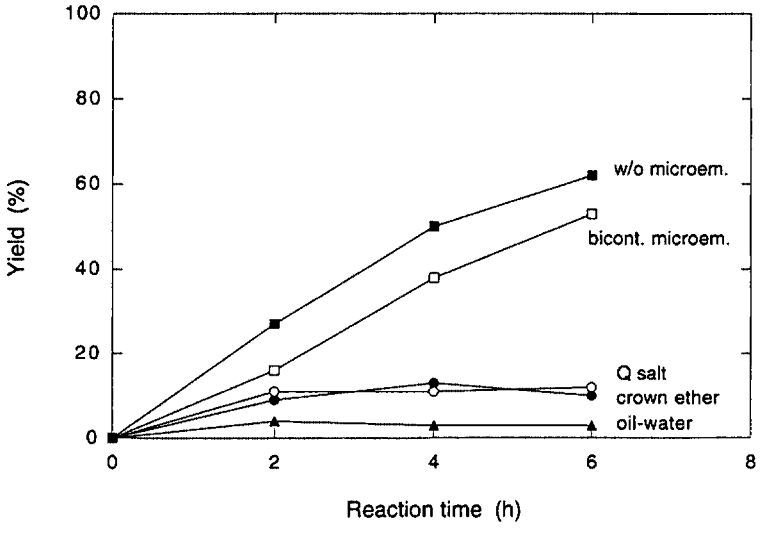


Figure 4. Reaction profiles for decyl sulfonate synthesis in two microemulsions (one water-in-oil and one bicontinuous) and three two-phase systems (one with added Q salt, one with added crown ether and one without phase-transfer agent).

interface of the microemulsion. For instance, epoxidation of styrene in a two-phase system gave 40% enantiomeric excess while the same reaction using the same enantiomerically pure catalyst gave 27% enantiomeric excess.

Rusling has explored the use of microemulsions as media for electroorganic synthesis.[14,15] The reason for the interest in using microemulsions for such reactions is the same as in many other instances: water is a poor solvent for many of the substrates used in these processes and microemulsions are an alternative to the aprotic organic solvents that are otherwise the reaction medium of choice. Synthetic applications include dehalogenations, carbon–carbon bond formation and cyclisation reactions. A recent example of a cyclisation reaction involves formation of trans-1-decalone by ring closure of *n*-bromoalkyl-2-cyclohexenones using a metallopolyion film of cobalt corrin vitamin B_{12} hexacarboxylate attached to carbon electrodes.[16]

Microemulsions have been used as media for hydroformylation reactions.[17] Water-soluble rhodium complexes were found to be highly active in microemulsions based on fatty alcohol ethoxylates. A series of internal olefins have been hydroformylated at temperatures of around 120 °C and a pressure of 100 bar. 7-Tetradecene as model alkene was hydroformulated to give 2-hexylnonal with high reaction rate and with a high degree of regioselectivity. It was also shown that the catalyst could be recycled in the work-up process. In a very recent work the same concept of compartmentalizing the medium for a rhodium-catalyzed reaction has been applied to a carbon–carbon bond coupling of Heck-type.[18] Instead of using surfactant self-assemblies to create the water pools in which the metal–organic catalyst resided, mesoporous silica, made via self-assembled surfactants as template, was used. The porous material was filled with an aqueous solution of the water-soluble catalyst and was kept dispersed in a solution of the hydrophobic substrates in a hydrocarbon solvent. The reaction proceeded in good yield.

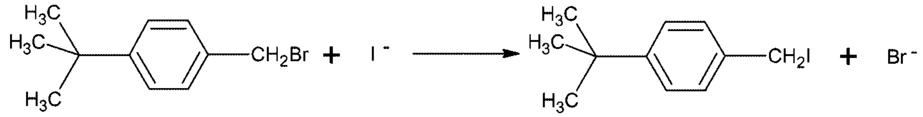
Caron et al. have used microemulsions as reaction media to carry out oxidation of hydrophobic substances using singlet oxygen, generated from molybdate-catalyzed decomposition of hydrogen peroxide, as oxidizing agent.[19] The water generated during the reaction will be a problem because it will eventually lead to phase separation of the system. In order to keep the water content at a low and fairly constant level, the reaction mixture was circulated through a ceramic membrane module that partially dewatered the microemulsion. The membrane showed good retention for the oil and the surfactant, as well as for the hydrophobic reactant and the catalyst. This is an interesting technique that may be generally applicable to microemulsion-based processes in which water is generated.

Surfactants form liquid crystalline phases at high concentration and such systems have also been explored as media for organic synthesis. Reactions in microemulsions have been compared with reactions in liquid crystalline phases. Such comparisons are interesting because they may give information about what is most important for the high reactivity of microemulsion systems: the large oil-water interface or the high dynamics of the system. Liquid crystalline phases have a somewhat higher internal interfacial area than microemulsions but liquid crystals lack the high dynamics of microemulsions. Formation of 2-furfurylthiol from cysteine/furfural and cysteine/ribose mixtures proceeded much more rapidly in both water-in-oil microemulsions[20] and bicontinuous cubic phases[20,21] than in aqueous systems. The reaction was faster in the cubic phase than in the microemulsion, a fact that was attributed to the larger interfacial area in the former system.[21]

In another comparison between a liquid crystalline phase and a microemulsion as reaction medium an amphiphilic polymer, a poly(ethylene glycol) with hydrophobic chains at both ends, was synthesized in an oil-in-water microemulsion and in a lamellar liquid crystal. Both systems were based on penta(ethylene glycol)monododecyl ether ($C_{12}E_5$) as surfactant and decane as oil component. Using the same composition and changing only the temperature one could go from a microemulsion (at 22 °C) to a lamellar liquid crystalline phase (at 39 °C). Thus, in this case the interfacial area, which is largely determined by the surfactant content, was about the same in the two systems. The reaction rates in the two systems were approximately the same and very much higher than the rate of the same reaction performed in a two-phase system without neither surfactant, nor phase-transfer agent.[22]

Figure 5 shows results from a detailed investigation of reaction rates in different types of microheterogeneous media: two liquid crystalline phases, slurries of two mesoporous materials with corresponding geometry, and one $C_{12}E_5$-based microemulsion.[23] The reaction studied is a nucleophilic substitution reaction, reaction of 4-*tert*-butylbenzyl bromide with potassium iodide. As can be seen from the Figure, the reaction was extremely fast in the two liquid crystalline phases, intermediate in the slurries of mesoporous materials and somewhat slower – although still fast compared to the two-phase system – in the microemulsion. Thus, judging from the reported comparisons between reactions in surfactant liquid crystalline systems and in microemulsions it seems that the rate is faster or as fast in the liquid crystalline phases as in the microemulsions. One may then conclude that the large interfacial area is the decisive factor for the reactivity in the reaction media based on self-assembled surfactant and that the high dynamics of microemulsions is not important.

In another study the same reaction was investigated in different types of microemulsion media, all based on nonionic surfactants of fatty alcohol ethoxylate type.[24] An interesting result from that study was that the rate in a Winsor I system is very similar to that in the one-phase microemulsion. As was discussed in the section "Microemulsions", a Winsor I system is a two-phase system consisting of an oil-in-water microemulsion in equilibrium with excess oil. It was also shown that it was not necessary to stir the Winsor system. The rate with and without stirring was the same. The observation that a Winsor system is just as effective a reaction medium as a one-phase microemulsion has been observed before, for another nucleophilic substitution



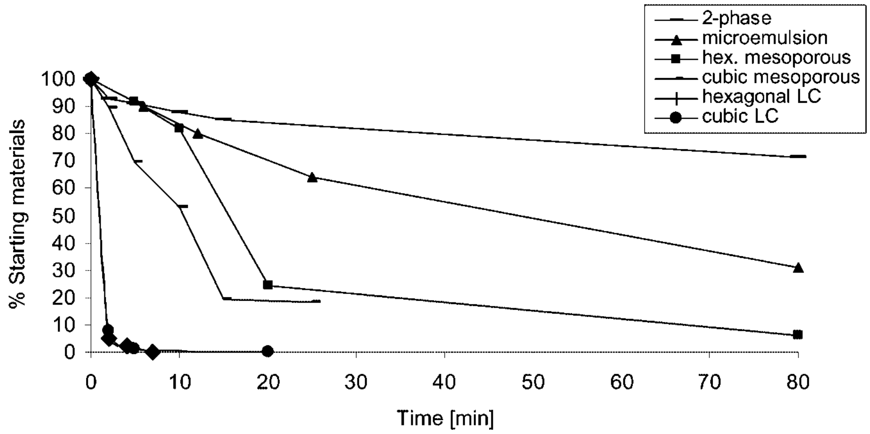


Figure 5. Reaction profiles for reaction between 4-*tert*-butylbenzyl bromide and potassium iodide using a 1:10 molar ratio of the reactants. The reactions were performed in a hexagonal or cubic liquid crystalline phases, in slurries of finely divided mesoporous silica with hexagonal or cubic geometry, in a microemulsion, and in a decane/water two-phase system.

reaction.[25] The fact that a Winsor I system can be used instead of a one-phase microemulsion is practically important. Formulation of a one-phase microemulsion is often a problem, particularly when one wants a high loading of reactants into the oil and water domains, and one may end up with various types of two- or three-phase systems. Evidently, such systems may be just as useful as reaction media, as long as one of the phases is a microemulsion. The excess phase (or phases) can be regarded as reservoirs for the reactant (or reactants) while the reaction occurs at the oil-water interface of the microemulsion phase.

In the same study it was also shown that reaction in a micellar system, i.e., with the lipophilic reactant, 4-*tert*-butylbenzyl bromide, solubilized in the nonionic surfactant micelles, was somewhat faster than the reactions in a one-phase microemulsion and the Winsor I system. Again, this is likely to be due to the difference in interfacial area. The micellar system, which consisted only of surfactant and water together with the reactants, had even higher interfacial area than the microemulsions, in which the apolar domains have been enlarged by the oil component.

4. Microemulsion Catalysis

It is well-known that reactions involving attack by a charged reactant on a reactant of different charge that has self-assembled into micelles often occur faster than when the same reaction occurs between the free species in bulk. A typical example is alkaline hydrolysis of surface active cationic esters. The reason for the rate acceleration is that the micelles of cationic ester-containing surfactants will attract counterions. Negatively charged ions, including hydroxy ions, will therefore accumulate around the micelle. This will lead to a higher pH in the vicinity of the micelles than in bulk. This type of rate acceleration, pioneered by Bunton, is called micellar catalysis.[26]

The same effect can be seen for microemulsions and the term microemulsion catalysis has been used for the phenomenon. There are many examples of how the charge of the surfactant headgroup can affect the rate of reaction between a lipophilic organic molecule and a charged, polar nucleophile. The general rule is that cationic surfactants accelerate the reaction involving anionic nucleophiles and vice versa. However, it has been found that for cationic surfactants the choice of counterion is decisive of the rate. The choice of counterion for anionic surfactants seems to be of less importance. The fact that anions interact more strongly with oil-water interfaces than cations is well known and the magnitude of the interaction of different anions follows the so-called Hofmeister series.[27]

It has been shown that the addition of a small amount of the anionic surfactant sodium dodecyl sulfate (SDS) to a nonionics-based microemulsion decreased the rate of decyl sulfonate formation from decyl bromide and sodium sulfite.[28] Addition of minor amounts of the cationic surfactant tetradecyltrimethylammonium salt gave either a rate increase or a rate decrease depending on the surfactant counterion. A poorly polarizable counterion, such as acetate, accelerated the reaction. A large polarizable counterion, such as bromide, gave a slight decrease in reaction rate. The reaction profiles for the different systems are shown in Figure 6.

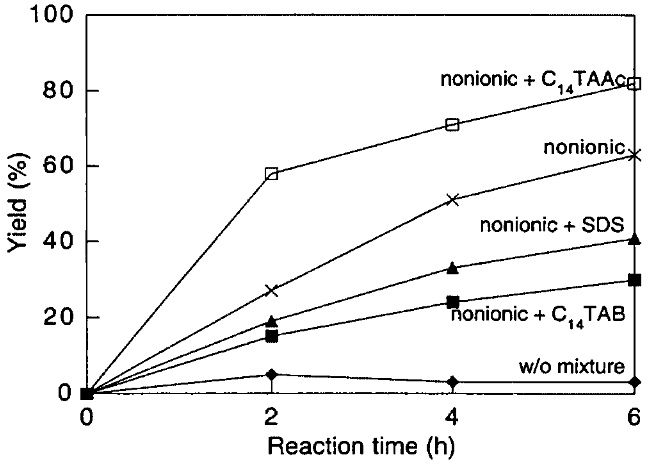


Figure 6. Effect of addition of 2% of ionic surfactant to a microemulsion based on a nonionic surfactant on the rate of formation of decyl sulfonate from decyl bromide and sodium sulfite. The anionic surfactant is sodium dodecyl sulfate (SDS). The cationic surfactant is a tetradecyltrimethylammonium salt with either acetate (C_{14}TAAc) or bromide (C_{14}TAB) as counterion.

The effect of surfactant charge on the reaction rate was investigated for the ring opening of 1,2-epoxyoctane with sodium hydrogen sulfite.[29] The reaction, which was performed in a Winsor III microemulsion, i.e., a microemulsion in equilibrium with both oil and water, was fast when a nonionic surfactant was used as the sole surfactant and considerably more sluggish when a small amount of SDS was added to the formulation. Another reaction in which the effect of added ionic surfactant was studied related to oxidation of azo dyes by hydrogen peroxide catalyzed by manganese porphyrins. The reaction was fast in a microemulsion based on nonionic surfactant. Addition of a small amount of cationic surfactant speeded up the reaction further while addition of an anionic surfactant lead to retardation.[30] These results imply that an anionic species is involved in the rate-determining step of the reaction.

An interesting example of a specific ion effect in microemulsions is the strong increase in reactivity found for large, polarizable anions such as iodide and bromide. The tendency for such ions to interact with, and accumulate at, the interface can be taken advantage of for preparative purposes. The increased concentration of such ions in the interfacial zone, where the reaction takes place, will lead to an increase in reaction rate. Expressed differently, the reactivity of iodide and other highly polarizable ions will be very high in such systems. A halide ion may also inhibit a reaction by competing with a more reactive anion. The microemulsions need not be based on cationic surfactants that would drive the anions to the interface by electrostatic attraction. Also microemulsions based on nonionic surfactants display the effect because large, polarizable anions interact with the hydrophobic surface by dispersion forces.[31,32] The mechanism of attraction (and the rationale for the increased concentration of reacting species) is, thus, different from that of micellar catalysis, which is basically an ion exchange process.

An illustrative example of the effect of a large polarizable ion at the oil-water interface is the above-mentioned reaction between 4-*tert*-butylbenzyl bromide and potassium iodide to give 4-*tert*-butylbenzyl iodide. The reaction was performed in a microemulsion based on the nonionic surfactant penta(ethylene glycol)monododecyl ether ($C_{12}E_5$) and the temperature was varied from 23 to 29 °C, which is the total temperature range of the isotropic oil-in-water region of this system.[33] It was found that the reaction rate decreased considerably when the temperature was increased from 23 to 29 °C. ^{125}I NMR showed a marked temperature effect on line broadening; the lower the temperature the broader the signals (within the temperature range 23 to 29 °C). This indicates that the iodide ion interacts more strongly with the interface at lower temperature, which is likely to be the reason for the inverse temperature-reactivity relationship. Thus, ion binding to the microemulsion interface can have a pronounced effect on reactivity also in microemulsions based on uncharged surfactants. In another investigation of a nucleophilic substitution reaction in microemulsion, synthesis of 1-phenoxyoctane from 1-bromooctane and sodium phenoxide, no accumulation of the nucleophile at the interface could be observed based on the kinetics data.[25,34] This is in line with the view that only the large polarizable anions, such as iodide, become attracted to the interface due to dispersion force interactions.[31]

Thus, the use of microemulsions as media for organic substitution reactions can lead to a difference in reaction pattern due to differences in relative nucleophilicity as compared to reactions in homogeneous media. Bunton, Savelli and others have shown this to be the case for reactions in micellar media.[26,35–38] For instance, the type of reaction medium – homogeneous solution or micellar solution based on cationic surfactant – has been found to be decisive of the reaction of sulfonate esters in the presence of equimolar amounts of bromide and hydroxy ions. Without surfactant present attack by hydroxy ions dominates. In the micellar solutions, on the other hand, bromide is the dominating reacting species. Evidently, the larger and more polarizable bromide ion becomes more attracted than the hydroxy ion to the micellar interface.[35]

The character of the oil used in the microemulsion formulation may also affect the reaction at the interface. This was investigated in a recent work using a chemical reaction, hydrolysis of anisoyl chloride, as a probe.[39] Anisoyl chloride is oil soluble and slightly polar. It can be expected to partition between the oil domain and the interface and the hydrolysis reaction will only occur at the interface. A water-in-oil microemulsion was formulated with an anionic surfactant and a range of organic solvents were explored as oil component. ^{1}H NMR was used to study the nature of the water in the system and it was found that the amount of free water varied with the hydrocarbon's ability to penetrate the surfactant palisade layer, the stronger penetration the smaller the amount of free water in the system. It was found that the reaction rate decreased with increasing oil penetration. The net effect was that the hydrolysis reaction proceeded faster with alicyclic hydrocarbons than with cyclic hydrocarbons and that smaller alicyclic hydrocarbons gave faster reaction than longer homologues.

5. Combining the Microemulsion Approach with Phase-Transfer Catalysis

Microemulsions and two-phase systems with added phase-transfer agent are both useful means of overcoming reagent incompatibility, but on entirely different accounts. In phase-transfer catalysis, the nucleophilic reagent is carried into the organic phase where it becomes poorly solvated and highly reactive. In the microemulsion approach there is no transfer of reagent from one environment to another; the success of the method relies on the very large oil-water interface at which the reaction occurs. In an attempt to combine the two methods and take advantage of both the high reactivity of a poorly solvated anion in phase-transfer catalysis and the very large oil-water interface of a microemulsion, ring-opening of a lipophilic epoxide was carried out in a microemulsion in the presence of a conventional Q salt, tetrabutylammonium hydrogen sulfate.[5] Reactions were also performed in a two-phase system with and without added Q salt. It was found that the rate of the Q salt-catalyzed system is increased further when the reaction is carried out in a microemulsion instead of an oil-water two-phase system.

The above reaction was performed in a microemulsion based on a chlorinated hydrocarbon and a combination of two alkyl glucoside surfactants was used for formulating the microemulsion. An attempt was also made to accelerate the same reaction performed in a microemulsion based on water, nonionic surfactant and hydrocarbon oil.[29] The reaction was performed in a Winsor III system and the same Q salt, tetrabutylammonium hydrogen sulfate, was added to the formulation. In this case the addition of the phase-transfer agent gave only a marginal increase in reaction rate. Similar results had previously been reported for an alkylation reaction performed in different types of micellar media.[40] The addition of a Q salt gave no effect for a system based on cationic surfactant, a marginal increase in rate for a system based on nonionic surfactant and a substantial effect when an anionic surfactant was used. The last system, also with Q salt added, gave lower yield than the first two, however, most likely due to electrostatic repulsion of the negatively charged nucleophile by the anionic micelles.

The microemulsion approach and phase-transfer catalysis was combined in another nucleophilic substitution, reaction between 4-*tert*-butylbenzyl bromide and potassium iodide.[41] The microemulsion was based on a chlorinated hydrocarbon and a sugar surfactant, octyl glucoside, which means that there were no counterions competing with the nucleophile at the oil-water interface. A quaternary ammonium salt, tetrabutylammonium hydrogen sulfate, was used as phase-transfer catalyst, both in an amount equimolar to the iodide and in a catalytic amount. The results are shown in Figure 7. As can be seen, the combined approach gives the highest reaction rate in both cases.

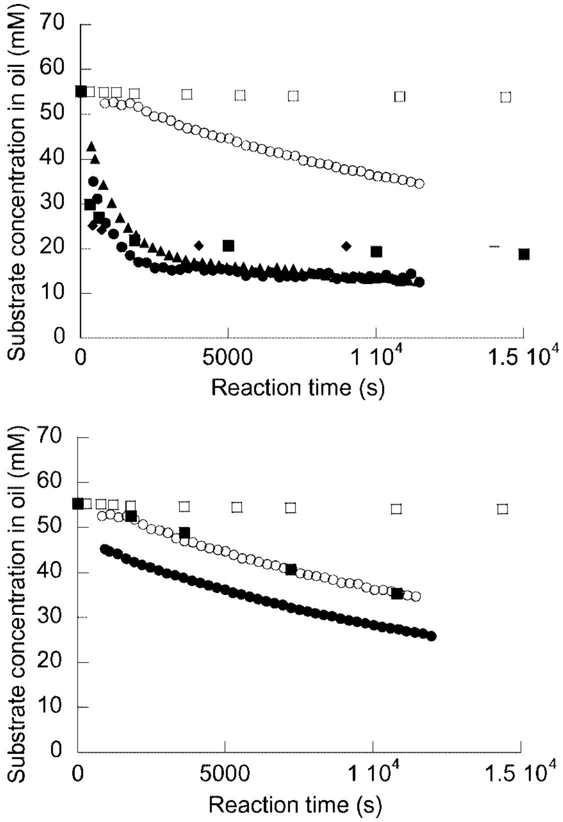


Figure 7. Reaction profiles for the reaction between 4-*tert*-butylbenzyl bromide and potassium iodide in microemulsion based on dichloromethane, octyl glucoside and deuterated water using either an equimolar (top) or a catalytic (bottom) amount of tetrabutylammonium hydrogen sulfate (TBAHS) or tetrabutylammonium bromide (TBAB) as phase-transfer agent. The reaction was monitored by NMR observing the disappearance of the $–CH_2Br$ signal and appearance of the CH_2I signal. Top: in D_2O/C_8G_1-CH_2Cl_2: (○) without Q salt, (●) with TBAHS, (▲) with TBAB; and in D_2O/CH_2Cl_2: (■) without Q salt, (■) with TBAHS, (♦) with TBAB. Bottom: in D_2O/C_8G_1-CH_2Cl_2: (○) without Q salt, (●) with TBAHS; and in D_2O/CH_2Cl_2 (□) without Q salt, (■) with TBAHS.

In a recent work microemulsions based on nonionic surfactants with and without added phase-transfer agent (PTA) was used as media for epoxidation of α,β-unsaturated enones with alkaline hydrogen peroxide.[42] Figure 8 shows the reaction for one of the enones used, *trans*-chalcone. When a fatty alcohol ethoxylate was used as surfactant the reaction rate increased according to: two-phase system << two-phase system with added PTA < microemulsion < microemulsion with added PTA. The outcome was slightly different when the fatty alcohol ethoxylate was replaced by another nonionic surfactant, an alkyl-β-D-glucopyranoside. The reaction in microemulsion was then twice as fast as in the previous system but addition of the PTA did not increase the rate further.

The higher reactivity in the microemulsion based on the glucoside surfactant compared to the microemulsion based on the fatty alcohol ethoxylate was explained as an effect of the difference in dielectric constant at the oil-water interfaces of the two systems. It is known that the dielectric con-

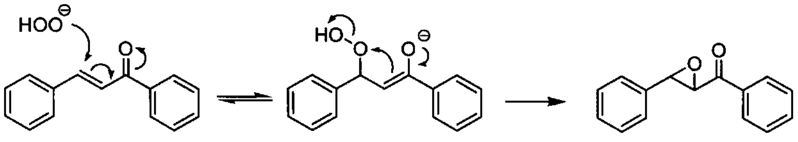


Figure 8. Oxidation of *trans*-chalcone by alkaline hydrogen peroxide (redrawn from ref.[42]).

stant in the interfacial layer built up by a glucoside surfactant is higher than in the interfacial layer of an alcohol ethoxylate.[43] This is due to the fact that the sugar head group of the former surfactant is more polar than the oligo(ethylene glycol) head group of the latter surfactant. As shown in Figure 8, the conversion of *trans*-chalcone to the epoxide proceeds via a negatively charged intermediate. This intermediate is most likely better stabilized the more polar the reaction zone.

The difference in polarity of the interfacial zones of microemulsions based on either a glucoside surfactant or a fatty alcohol ethoxylate has previously been used to explain the difference in reactivity obtained in the above-mentioned reaction between 4-*tert*-butylbenzyl bromide and potassium iodide. For this reaction the rate was higher with a fatty alcohol ethoxylate than with an alkyl glucoside as microemulsion surfactant.[33] It is assumed that this is a S_N2 reaction involving a charged nucleophile and a transition state with dispersed charge, which can be written as $Br^{\delta-}$---R---$I^{\delta-}$, where R is 4-*tert*-butylbenzyl. It is known that such reactions proceed slower the more polar the reaction medium.[44] It is also known that for such reactions the transition state is more solvated in polar aprotic solvents than in protic ones, while the starting nucleophile, in this case the iodide ion, is less solvated in aprotic solvents. This factor should not be of importance here, however, because both microemulsions use water as polar solvent. (Nucleophilic substitution at a benzylic carbon may, in fact, also be of S_N1 character, which would make the solvent effect different. However, with a powerful nucleophile such as the iodide anion it is like that the S_N2 character dominates.)

6. Inducing Regioselectivity

The large oil-water interface of microemulsions can be used as a template for organic reactions. Organic molecules with one more polar and one less polar end will accumulate at the oil-water interface of microemulsions. They will orient at the interface so that the polar part of the molecule extends into the water domain and the nonpolar part extends into the hydrocarbon domain. This tendency for orientation at the interface can be taken advantage of to induce regiospecificity of an organic reaction. A water-soluble reagent will react from the "water side", i.e., attack the polar part of the amphiphilic molecule, and a reagent soluble in hydrocarbon will react at the other end of the amphiphilic molecule. The principle has previously been applied to a micellar system for controlling regioselectivity of a Diels–Alder reaction in which both reactants were surface active.[45,46] When the reactions were run in an organic solvent, i.e., in absence of micellar orientational effects, the two regioisomers were obtained in equal amounts. When, on the other hand, the reactions were carried out in an aqueous buffer in which the reactants form mixed micelles, a regioisomer ratio of 3 was obtained.

It has recently been found that microemulsions can be used as a tool to differentiate between the first and the second step of a substitution of symmetrical bifunctional reactants, in this case α,ω-dibromoalkanes.[47] In a homogeneous system with good solubilizing capacity for both the lipophilic reactant, the α,ω-dibromoalkane, and the hydrophilic reactant, sodium sulfite, the two substitution steps occur at the same rate. The situation proved to be different in a microemulsion. The intermediate mono-substituted species, a bromoalkanesulfonate, has one polar and one nonpolar end; hence, it orients at the interface such that the sulfonate end points into the water domain, leaving the bromo end in the nonpolar environment. Provided that the alignment of the intermediate is fast compared to the rate of the substitution reaction, such an orientation of the intermediate may protect it from further nucleophilic attack. This turned out to be the case for some of the α,ω-dibromoalkanes. For the species with the shortest alkane chain, 1,4-dibromobutane, there was a pronounced difference in rate between the first and the second substitution step and the intermediate, bromobutanesulfonate could be recovered in high yield. The selectivity decreased with the alkane chain length. Evidently, the second bromide is less protected for the longer derivatives. A likely explanation for the effect is illustrated in Figure 9. The more limited regiochemical control for the longer derivatives is probably due to a considerable conformational freedom of these molecules, which allows the remaining bromomethyl group to be exposed at the interface. When the "spacer group" between the sulfonate and the bromomethyl group is short, such folding is more difficult to achieve.

The regiospecificity of electrophilic aromatic substitution reactions can be controlled by use of the oil-water interface of a microemulsion as template for the aromatic moiety. Bromination of two phenols and two anisoles has been carried out in a cationic surfactant-based microemulsion using the surfactant counterion, i.e., bromide, as reagent.[48] The bromide ion was oxidized to elemental bromine by dilute nitric acid, which in turn reacted with the aromatic compound. The results have been compared with two-phase procedures using either an in situ-prepared or a pre-prepared complex between bromine and a quaternary ammonium salt as oxidizing reagent and also with conventional

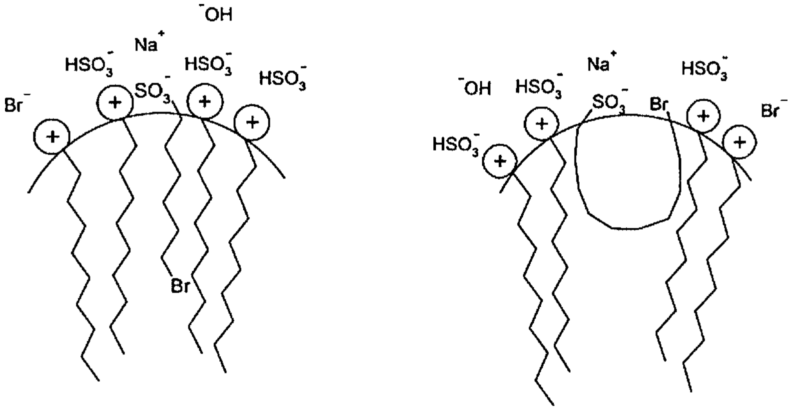


Figure 9. Alignment of a short-chain (left) and a long-chain (right) bromoalkanesulfonate at the oil-water interface of a microemulsion.

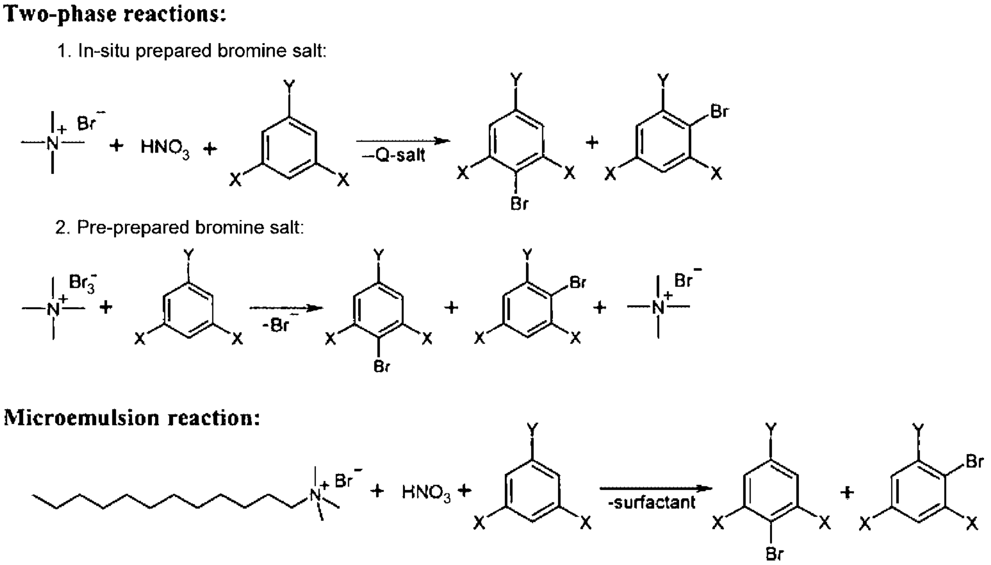


Figure 10. Reaction approaches used for bromination; X = H or CH_3; Y = CH_3, OH or OCH_3.

bromination using elemental bromine. The different routes are shown in Figure 10. Reaction in the microemulsion gave a more selective *para*-bromination than the other procedures. In addition, the microemulsion-based reaction proceeded smoothly at room temperature.

7. Work-Up Aspects

An inherent drawback with the use of microemulsions as media for organic reactions is that separation of the surfactant from the product may be a tedious process. In rare cases, such as in the synthesis of decyl sulfonate described in section "Overcoming reactant incompatibility", the product formed is a surface active compound and can be used as microemulsion surfactant in the next run. Then the work-up becomes easy. However, in the majority of cases there is a need to remove the surfactant from the end product and this is often a nontrivial issue because of the surfactant's pronounced tendency to generate foams and emulsions and to adsorb at all available surfaces, including those in chromatography columns. Different approaches have been proposed for removal of the surfactants and two of these will briefly be outlined here.

1. *Use of cleavable surfactants.* These are surfactants with built-in weak bonds, intended for decomposition at some point in a process. For instance, the surfactant may contain a betaine ester bond, in which case it readily breaks down into non-surface active products already at slightly alkaline conditions, it may contain an ortho ester bond, rendering it labile to acid, or it may contain an azo bond so that it decomposes under UV irradiation.[49] Use of a cleavable surfactant to create the microemulsion and adjusting the conditions after completed reaction so that the surfactant decomposes is an efficient way to eliminate the problem of separating the product from the surfactant. The breakdown products will not be surface active and will usually not cause problems in the further work-up process, such as chromatographic separation. However, the procedure is costly on large-scale operations because the surfactant is consumed in the process.

2. *Use of a Winsor system as reaction medium*. As mentioned above, Winsor systems, i.e., two- or three-phase systems in which a microemulsion is in equilibrium with an excess phase of water, of oil, or of both oil and water, can be used as reaction media. If a nonionic surfactant of fatty alcohol ethoxylate type is used as amphiphile, one can go from Winsor I, via Winsor III to Winsor II by increasing the temperature and the transition is reversible. Whereas the surfactant will always reside in the microemulsion phase, the product is likely to partition into an excess oil phase if it is an apolar substance and in an excess water phase if it is a polar compound. The principle is illustrated in Figure 11.[50] Hydrolysis of a lipophilic ester was performed in a Winsor I system (an oil-in-water microemulsion in equilibrium with excess oil.) The ester partitions between the excess oil phase and the oil droplets and the hydroxy ions reside in the continuous water domain of the microemulsion. The reaction takes place at the interface. After completed reaction acid as added to protonate the alkanoate formed and the temperature is raised so that a Winsor I to Winsor III transition occurs. The lipophilic products, a fatty acid and an alcohol, will predominantly partition into the oil phase and the surfactant will predominantly reside in the middle phase, which is a bicontinuous microemulsion. The same approach had previously been taken by Schubert et al. for the purification of nonionic surfactants.[51]

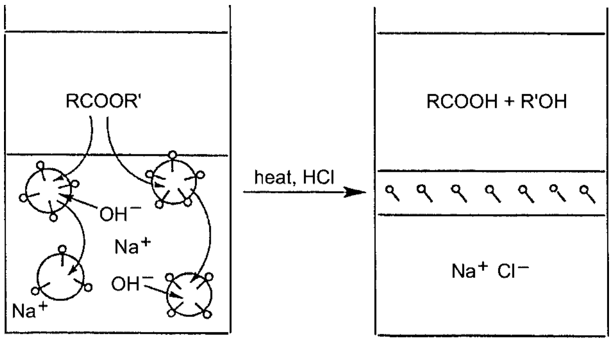


Figure 11. Ester hydrolysis in a Winsor I system followed by a heat-induced transition to a Winsor III system.

8. Conclusions

This review has attempted to show that microemulsions are highly useful as media for organic reactions involving one polar and one apolar reactant. The microemulsion approach to such reactions should be seen as an alternative to phase-transfer catalysis but the reaction principle is very different. In phase-transfer catalysis the water soluble species, often a nucleophile, is extracted into the organic phase by the help of a phase-transfer agent. In the microemulsion there is no transport of reactant from one phase into another; instead, the reactants meet at the interface, which is extremely large. The review also demonstrates that the two approaches can be combined, in which case a very high reactivity is obtained.

Many reactants align at the oil-water interface and microemulsions can then be used as a way to induce regioselectivity. Examples include electrophilic aromatic substitution and nucleophilic aliphatic substitution reactions, illustrating that the concept is of general nature.

The use of microemulsions as a tool for organic synthesis has attracted considerable attention in recent years and the topic has been reviewed before, see ref.[52–55]. These reviews have been published in surface chemistry journals. The present review was intended for the organic chemist and was therefore written in a somewhat different style.

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