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Microemulsions in Technical Processes

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I. Introduction

The term "microemulsion" was introduced by the English chemist J. H. Schulman. In 1943 he described the transition from a stable oil-rich mixture to a stable water-rich mixture and introduced the term "micro emulsion" for these systems in 1959.[1,2] Since then, the number of publications on this topic has continuously grown and microemulsions have attained increasing significance both in basic research and in industry. They offer a high potential for numerous practical applications due to their special properties.

The aim of this review is to present once again the basic properties of microemulsions and to relate them to some already established applications and also to show further potential fields of application. This review will survey this area, focusing mainly on the last decade. Earlier publications on the technical relevance of microemulsions and reverse micelles were reviewed by Langevin in 1982.[3]

The most important properties of these systems, which are of significance for technical applications, will be described in the parts II.A–C. Some of these properties are illustrated by schematic representations, but they are based on many measurements performed by numerous groups worldwide. Section II is rather concise presenting only those properties which are important for application while referring to more detailed reviews in all other respects.

II. Basic Properties of Microemulsions

A. What Are Microemulsions?

When water is mixed with an organic liquid immiscible with water and an amphiphile, generally a turbid milky emulsion is obtained which, after some time, separates again into an aqueous and an organic phase. Schulman observed in the 1950s that these turbid unstable emulsions can be converted into optically transparent and thermodynamically stable mixtures by adding alcohol. He was the first to use the term "microemulsion" for these stable mixtures containing two components which are not miscible by themselves, i.e. water and oil.[2] In the 1970s and 1980s, in-depth studies of mixtures of oil, water, and amphiphiles were carried out, since enhanced oil recovery required precise knowledge and understanding of the phase diagrams of these mixtures.[4-8] At present, the phase equilibria of mixtures of water, organic liquids, and amphiphiles may be regarded as well understood.[9-14] However, the internal structures of the variety of phases existing in water–oil–amphiphile systems is not yet well identified.

The interest of basic research is currently directed toward the development of a thermodynamic model describing the phase diagrams on the basis of the molecular interactions of the components involved.[15-18] In addition to thermodynamics, the structure[19-26] and dynamics of microemulsions are intensively studied.[27-32]

Figure 1 shows schematically the one-phase region of a ternary mixture of water, an alkane, and a nonionic amphiphile as a function of composition and temperature. At constant amphiphile concentration, a channel of homogeneous isotropic solutions is found

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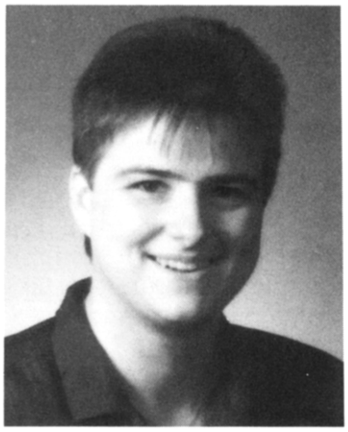
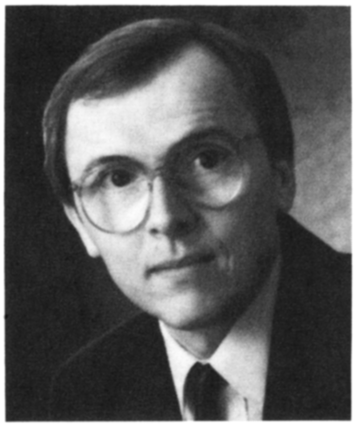
Milan Johann Schwuger (born in 1938) studied chemistry at the Rheinisch-Westfalische Technische Hochschule in Aachen and received his Ph.D. 1966. The Ph.D. thesis was in the field of "Adsorption/Desorption kinetics in aquious solutions". In 1966 he joined Henkel company in Düsseldorf. From 1966 to 1977 he was responsible for different interdisciplinary projects of the company. From 1977 to 1989 he was head of the physical chemistry research in the company. For his development of zeolite containing phosphate free detergents he received 1979 the Steinkopff-Award. Parallel habilitation at the University of Düsseldorf was finished 1984. In 1989 he was appointed as director of the Institute of Applied Physical Chemistry of the Research Center in Jülich and full professor of Applied Physical Chemistry at the University of Dusseldorf. At present he is president of the Kolloid-Gesellschaft in Germany.



Katrin Stickdorn (born in 1960) studied chemistry at the University of Bielefeld. She recieved her Diploma in 1986 and her Doctoral Degree in Physical Chemistry in 1990, both under supervision of Professor W. Knoche at the University of Bielefeld. Parts of her advanced studies on organic reactions in microemulsions she performed at the University of Santiago de Compostela, Spain, with Professor M. A. Lopez Quintela. In 1991 she started a postdoctoral fellowship at the Institut for Applied Physical Chemistry of the Reserch Centre Jülich, studying the synthesis of nanoparticles in microemulsions. In 1993 she joined the ICI Surfactants Technical Service group and concentrates her activities now on applications of surfactants in personal care.

in which the weight fraction, α, of the oil in the mixture of oil and water can be varied from 0 to 100%. This one-phase region is limited by two different two-phase regions. The macroscopically homogeneous mixtures are submicroscopically heterogeneous. The results obtained by investigations of the microstructure of these mixtures by light scattering experiments, electron microscopy, NMR self-diffusion, etc. are also shown schematically in Figure 1.$^{20-26}$

On the water-rich side, the mixtures consist of stable dispersions of oil droplets in water (o/w microemulsion), which coagulate with rising temperature. A spongelike structure is obtained if the



Reinhard Schomäcker (born in 1959) studied chemistry at the University of Bielefeld. He recieved his Diploma in 1984 and his Doctoral Degree in Physical Chemistry in 1987, both under supervision of Professor W. Knoche at the University of Bielefeld. Parts of his studies on mechanisms of chemical reactions in microemulsions were carried out with Professor B. H. Robinson at the University of Kent at Canterbury, England. In 1987 he joined the group of Professor M. Kahlweit at the Max-Planck-Institut for Biophysical Chemistry in Göttingen for studies on the thermodynamics and structures of microemulsions and lyotropic liquid crystals. In 1990 he finished a Habilitation thesis on organic synthesis in microemulsions. Also in 1990 he joined the chemical engineering group of the Central Research Laboratries of the Bayer AG in Leverkusen. Here he continues his research on applications of microemulsions as reaction media for chemical synthesis. Another part of his scientific activities are kinetic studies for the scaling up of chemical processes. In 1992 he completed his Habilitation for physical chemistry with Professor D. Woermann at the University of Cologne, where he gives lectures in colloid science, in addition to his appointment with the Bayer AG.

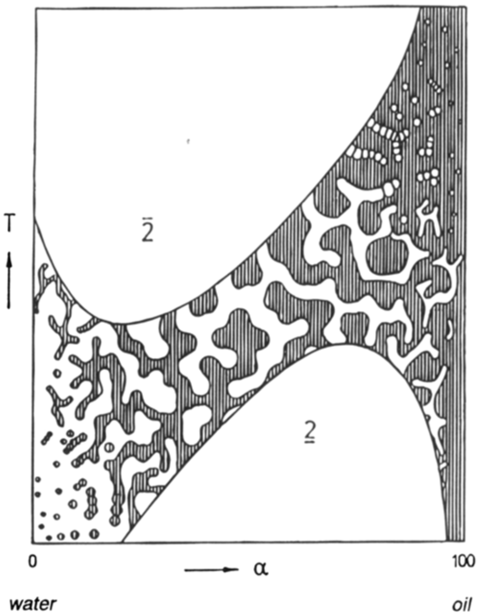


Figure 1. Schematic section of the phase prism of a ternary mixture of water, an organic liquid (oil), and a nonionic amphiphile. At constant amphiphile concentration, a region of isotropic single-phase solutions is observed extending from the water-rich to the oil-rich side of the phase prism. This single-phase region is surrounded by two two-phase regions in which the amphiphile is dissolved either in the aqueous bottom phase ($\underline{2}$) or in the organic top phase ($\bar{2}$). The hatching in the single-phase region illustrates the microstructure of the solutions.

mixtures contain approximately equal amounts of water and oil, i.e. if α = 30 to 70 wt %. The coherent domains of water and oil are about equal in size. On the oil-rich side, dispersed water droplets are found (w/o microemulsion), which coagulate with decreasing temperature. The size of the domains (in the range from 1 to 100 nm) is a function of amphiphile concentration and volume fractions of water and oil.[17,33] The interface between water and oil is covered by a monolayer of surfactant molecules. The size of the interface can be up to 10^5 m^2 per liter of microemulsion. In the two-phase region at lower temperatures ($\underline{2}$), an o/w microemulsion coexists with an almost pure oil phase. In the two-phase region at higher temperatures ($\bar{2}$), a w/o microemulsion coexists with an aqueous phase. The same pattern of structures described here for microemulsions with nonionic amphiphiles was reported by Chen and Strey for microemulsions with ionic amphiphiles.[34]

Since microemulsions contain both a polar component (water) and a nonpolar component (oil), they are capable of solubilizing a wide spectrum of substances. The mechanism of solubilization is similar to that in micellar solutions. The micelles are replaced by the oil domains which are capable of solubilizing all kind of hydrophobic substances. The solubilization of polar substances takes place analogously through the aqueous domains of the microemulsion. The solubilization capacity of microemulsions is generally much higher than that of micellar solutions.[35]

B. Phase Behavior of Microemulsions

Consider a ternary mixture of water (A), oil (B), and a nonionic amphiphile (C). A ternary mixture has four independant thermodynamic variables, namely temperature (T), pressure (p), and two composition variables. Since experiments have shown that the effect of pressure is small compared to that of temperature, pressure is kept constant at atmospheric level for this discussion. The phase behavior of the ternary mixture may then be represented exactly in an upright phase prism with the Gibbs triangle as base and temperature T as the ordinate (Figure 2). For the composition variables it is convenient to introduce the mass fraction α of oil in the mixture of water and oil

$$\alpha = \mathrm{B}/(\mathrm{A} + \mathrm{B})$$

and that of the amphiphile, γ, in the mixture of all three components

$$\gamma = \mathrm{C}/(\mathrm{A} + \mathrm{B} + \mathrm{C})$$

both expressed in weight percent (wt %). Each point in the phase prism is then unambiguously defined by a certain set of α, γ, and T.

Mixtures of water, oil, and nonionic amphiphile separate within a well-defined temperature interval into three liquid phases, an aqueous phase, an oil-rich, and an amphiphile-rich phase. In the amphiphile-rich phase the maximum mutual solubility between water and oil can be found, which is combined with a minimum of the interfacial tension between the water and oil phase. Both properties are the basis for applying microemulsions in various fields of science and technology. The origin of the three-phase triangle as well as that of the maximum in mutual solubility between water and oil were studied previously almost a century ago (for a review see ref 36). The three-phase triangle arises from the interactions between the miscibility gaps of the three corresponding binary mixtures representing the side planes of the phase prism. If each of the binary mixtures shows a miscibility gap at the temperature of the experiment, these gaps will extend into the prism, where they may overlap with each other. If they do, this will give rise to the coexistence of three liquid equillibrium phases.

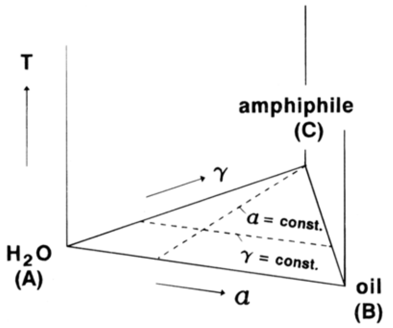


Figure 2. Phase prism with the Gibbs phase triangle as base and the temperature axis as ordinate.

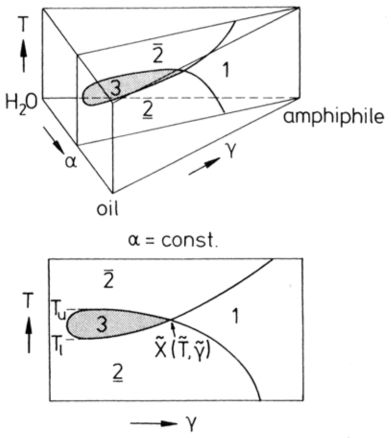


Figure 3. Schematic phase prism (top) of a ternary mixture of water, an organic liquid (oil) and a nonionic amphiphile. The essential information about the phase behavior is given by a vertical section of the prism describing phase behavior at constant α as a function of amphiphile concentration γ and temperature (bottom). At the mean temperature of the three-phase region, $\tilde{T}$, the lowest amphiphile concentration, $\tilde{\gamma}$, is required in order to enter the single-phase region.

The most convenient procedure for determining the position and extension of the three-phase region within the phase prism is to erect a vertical section through the prism at α = 50 wt % (Figure 3, top).

This is done by mixing equal masses of water and oil, then adding various amounts of amphiphlile, and observing the number of phases with rising temperature. At high concentrations of amphiphile a homogeneous mixture is observed between the melting and the boiling point. At somewhat lower concentrations the phase sequence is $\underline{2} \rightarrow 1 \rightarrow \bar{2}$, and at even lower concentrations the sequence is $\underline{2} \rightarrow 3 \rightarrow \bar{2}$ and finally, at very low concentrations two phases coexist at all temperatures. Plotting the results yields a pseudobinary phase diagram, as shown schematically in Figure 3 (bottom). The temperature interval where three phases are observed is limited by its lower temperature T_l and its upper temperature T_u. The determination of this pseudobinary phase diagram

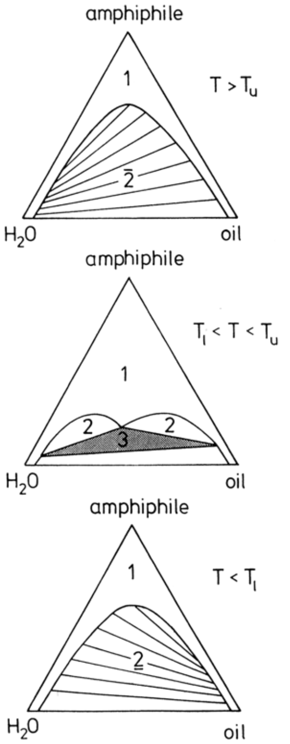


Figure 4. Isothermal sections of the phase prism at a temperature below the three-phase region (bottom), at the mean temperature of the three-phase region (middle), and at a temperature above the three-phase region (top).

may be handicapped by the appearance of lyotropic mesophases (L_α) at high amphiphile concentrations γ. Experience shows, however, that these mesophases disappear as one approaches the body of heterogeneous phases. The position of the three-phase body on the temperature scale may be characterized by its mean temperature

$$\tilde{T} = (T_1 + T_u)/2$$

whereas the efficiency of the amphiphile may be characterized by the concentration $\tilde{\gamma}$ needed to obtain a homogeneous mixture at $\tilde{T}$ and $\alpha = 50$ wt %. As can be seen in Figure 3 (bottom) the amount of amphipile needed to completely solubilize water and oil reaches a distinct minimum at $\tilde{T}$, whereas below and above this temperature the mutual solubility of water and oil is much lower, and therefore more amphiphile has to be added. This behavior varies very little with different amphiphiles. The two characteristic properties of the three-phase body, i.e. $\tilde{T}$ and $\tilde{\gamma}$, depend sensitively but systematically on the nature of both the oil and the amphiphile. In the two-phase region at lower temperatures the nonionic amphiphile is better soluble in water than in oil (signified by $\underline{2}$). Figure 4 (bottom) characterizes this situation by tie lines with a negative slope. At high temperatures the nonionic amphiphile is more oil soluble than water soluble (signified by $\bar{2}$ in Figure 4 (top) and by tie lines with a positive slope).

An isothermal section of the phase prism at a temperature within the three-phase interval is shown in Figure 4 (middle). This phase diagram is characterized by a much more extended one-phase region compared to that one of the isothermal sections at higher and lower temperatures. A simple explanation of this solubility change is that the solubilization of the amphiphile in water is driven by the formation of hydrogen bonds. These hydrogen bonds break with rising temperature, causing a better oil solubility of the amphiphile.

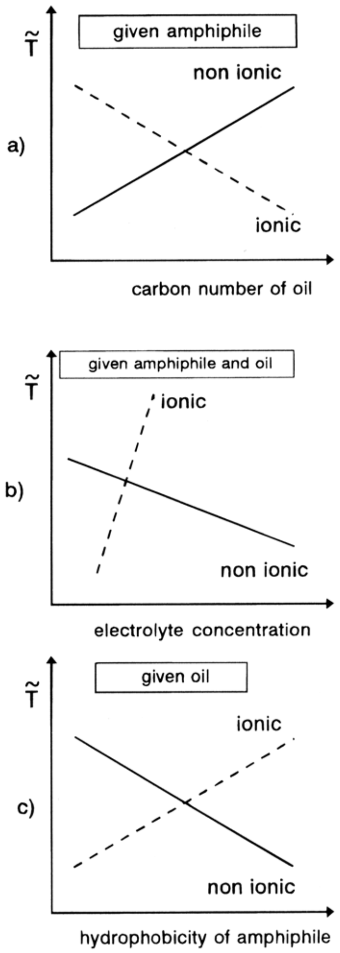


Figure 5. Dependence of $\tilde{T}$ on (a) the chain length of oil, (b) the electrolyte concentration of the microemulsion, and (c) the hydrophobicity of the amphiphile for ionic and nonionic amphiphiles.

This schematically described phase behavior is found in all mixtures of water, organic liquids, and nonionic amphiphiles. Therefore it is possible to find for almost any combination of water (or electrolyte solution) and organic liquid an amphiphile that stabilizes a microemulsion.

The temperature range in which microemulsions are formed is shifted systematically depending on the length of the alkyl or ethylene oxide chain of the amphiphile and the polarity of the organic liquid. These correlations as well as the influence of added electrolytes on the phase behavior of these mixtures are shown schematically in Figure 5.

In the diagram, the three-phase region is characterized by the mean temperature of the three-phase region, $\tilde{T}$. For a given amphiphile, the three-phase region is shifted toward higher temperatures with increasing chain length of the oil, i.e. with increasing hydrophobicity. If lyotropic electrolytes are added (e.g. NaCl, NaOH, KCl, Na_2SO_4, etc.), the three-phase region is shifted toward lower temperatures.[37] For a given organic liquid to be emulsified (oil), a displacement of the three-phase region toward lower temperatures is observed with increasing hydrophobicity of the amphiphile.

The same description of the phase behavior given here for mixtures with nonionic amphiphiles may be applied to mixtures with ionic amphiphiles, but with one essential difference. The solubility of ionic amphiphiles in water increases with rising temperature, therefore ionic amphiphile also show a change in preferred solubility, but from oil soluble to water soluble with rising temperature. Again, for the transition a three-phase region is crossed that exibits the same properties as the three-phase region of the nonionic systems.[14]

Figure 5 also shows the same dependences for mixtures with ionic amphiphiles. In all three cases, the curves depicting these effects are inverse for ionic and nonionic amphiphiles. For the detailed explanation of this behavior we refer to refs 13 and 14. For many applications of microemulsions the most important difference between ionic and nonionic amphiphiles is the signficantly lower electrolyte sensitivity of nonionic amphiphiles. The electrolytes reduce the solubility of the hydrophilic head groups of the amphiphiles in the water. In the case of nonionic amphiphiles they compete for the hydrating water of the head groups, an effect of minor influence on phase behavior. In the case of ionic amphiphiles, the electrostatic interactions between the charged head groups are strongly influenced by the addition of electrolytes so that the phase behavior is significantly changed.

Apart from the mean temperature of the three-phase region, $\tilde{T}$, the so-called phase inversion temperature (PIT) is frequently used in the literature for characterizing the properties of water–oil–surfactant systems. It characterizes the transition in the preferred solubility of the surfactant from water to oil solubility. In many systems, PIT corresponds to the mean temperature $\tilde{T}$. For very efficient systems only the PIT may be determined by a conductivity measurement, but it is not possible to determine $\tilde{T}$ by the method described above.[14] This is due to the fact that the three-phase region in such systems is often very small and difficult to determine since phase separation frequently takes a very long time.

The schematic diagrams shown so far do not provide any information about the concentrations of amphiphiles in the mixtures forming microemulsions. The characteristic value of a system, i.e. the amphiphile concentration $\tilde{\gamma}$ required to obtain a single-phase mixture with $\alpha = 50$ wt %, varies with the chain length of the amphiphiles. For amphiphiles of medium-chain length (e.g. C_6E_3 or C_8E_4) $\tilde{\gamma} \approx 15-30$ wt % if a microemulsion is to be produced from water and hydrocarbons with 6–12 carbon atoms.[38] For longer-chained amphiphiles (e.g. $C_{12}E_5$ or $C_{14}E_8$) $\tilde{\gamma} \approx 3-10$ wt % for the same hydrocarbons. Amphiphile efficiency thus increases with growing chain length. As a rule of thumb, $\tilde{T}$ changes only slightly if the structure of the nonionic amphiphile is changed from C_iE_j to $C_{i+2}E_{j+1}$ with constant chain length of the oil, e.g. from C_8E_4 to $C_{10}E_5$. More detailed reviews on phase behavior were published by Kahlweit.[13,14,36]

Part of the literature uses a nomenclature for phase behavior based on papers by Winsor. He distinguished between four types of microemulsions which we find again today in the different single-, two- and three-phase regions of the phase diagrams.[39]

C. Interfacial Tension between Water and Oil Phase, σ_{ab}

However, efficiency is not the only important feature of microemulsions. In cleaning processes and enhanced oil recovery, for example, the interfacial tension between aqueous solution and oil as well as wetting of the body to be cleaned by the solution plays an important role. There are indications that the radius of the dispersed droplets, r, is determined by the interfacial tension, σ_{ab}, between the solvent and the droplet.[17,40] The relation reads

$$\sigma_{ab} r^2 = k_B T \qquad (1)$$

where k_B denotes the Boltzmann constant. At room temperature, i.e. at about 300 K, $k_B T \approx 4 \times 10^{-18}$ mJ. This relation means the lower σ_{ab}, the greater is r. On the other hand, it is only meaningful to speak of "colloidal droplets" if r is significantly smaller than the wavelength of visible light (~400 nm). If, therefore, $r \approx 10$ nm is assumed in a rough calculation, it follows from relation 1, using these two values, that very low interfacial tensions of $\sigma_{ab} \approx 4 \times 10^{-2}$ mN m^{-1} would be required to attain a stable droplet of this radius. It is generally known that amphiphiles reduce the interfacial tension between water and oil ($\sigma \approx 50$ mN m^{-1}) considerably. Even more important, however, is that the interfacial tension σ_{ab} reaches a distinct minimum at the mean temperature of the three-phase region $\tilde{T}$.[17] This means that the efficiency of an amphiphile, $1/\tilde{\gamma}$, has a maximum at that temperature where the interfacial tension, σ_{ab}, has a minimum, which again underlines the significance of $\tilde{T}$. The lowest values of σ_{ab} measured at $\tilde{T}$ are in the range of 10^{-5} mN m^{-1} for ionic amphiphiles and 10^{-4} mN m^{-1} for nonionic amphiphiles.[41–43] An example of very low interfacial tensions of a system near $\tilde{T}$ is given in Figure 6.[44]

In his paper "Microemulsions—A thermodynamic approach"[17] Kahlweit describes the relations between $\tilde{T}$, $\tilde{\gamma}$, and σ_{ab} and shows that the minimum of σ_{ab} is a direct consequence of the temperature-depending form of the three-phase region.

A completely different approach describing the interfacial tension σ_{ab}, the associated structures and the phase behavior of microemulsions uses the physical description of the interfacial film of amphiphilic molecules exhibiting a spontaneous curvature r_o and a bending modulus k.[45–48] The following equation is obtained for the relation between droplet radius r and interfacial tension σ_{ab}:

$$\sigma_{ab} = k/(2 r r_o) \qquad (2)$$

A comparison of eqs 1 and 2 leads to the conclusion that k must be of the order of magnitude of $k_B T$.

These two relations describing the interfacial tension σ_{ab} illustrate very different approaches developing a model for the description of the thermodynamics and structure of microemulsions. In the first case, the approach focuses on the question of how the

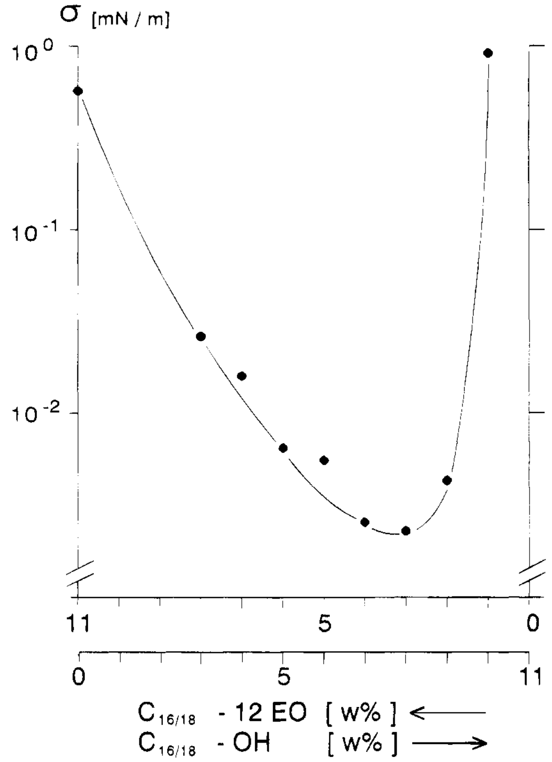


Figure 6. Interfacial tension between water and oil of a system near $\tilde{T}$. The system is water, paraffin oil, and a mixture of surfactant and cosurfactant at different ratios at a temperature of 75 °C.[44] The variation of the ratio between surfactant and cosurfactant causes a shift of the mean temperature of the overall system from a temperature above to a temperature below the temperature of the experiments (T = 75 °C).

interface of amphiphilic molecules is formed. What molecular interactions determine the value of the interfacial tension? In the second case, the interfacial film is assumed to be given and the question to answer is: what molecular interactions determine the value of r_0 and k? These questions show that extensive experimental and theoretical work is still required for the development of a model describing the thermodynamics and structure of microemulsions.

III. Applications

Microemulsions and reverse micellar systems are already applied in certain industrial fields, but there are also potential applications not yet established. In the following, we would like to outline certain processes and applications in order to demonstrate their significance and potential.

A. Enhanced Oil Recovery

Roughly 30% of the total content of an oil reservoir can be extracted today by primary recovery and flooding with water. Approximately another 20% can be obtained by enhanced oil recovery. A potential technique already applied today in pilot experiments, which will undoubtedly be increasingly employed in the future, is flooding with surfactants, microemulsions, and microemulsion–polymer systems. The method is based on the very low interfacial tensions and good wetting properties of these systems. It considerably enhances the mobilization of oil droplets or oil ganglions entrapped in the rock pores. The interfacial tension between crude oil and water is typically 50 mN m^{-1}, whereas values of 10^{-4} to 10^{-5} mN m^{-1} can be obtained in a suitable microemulsion system. Neumann[49] describes the processes during flooding by a triangular diagram, (shown in Figure 7). The system of oil "O", the water used for flooding "W", and surfactant "S" may be treated as a pseudoternary system although the oil phase itself is a complex mixture; the water is a solution of salts and the surfactant a mixture of various surface-active substances of technical quality. The phase triangle shows four different regions, which can be described as (I) single-phase region, microemulsion, type 4 according to Winsor,[39] (IIa) two-phase region, water phase and O/W microemulsion, type 2 according to Winsor, (IIb) two-phase region, oil phase and W/O microemulsion, type 1 according to Winsor, and (III) three-phase region, water phase, W, and oil phase, O, and microemulsion M, type 3 according to Winsor. Point M in Figure 7 denotes an isothermal invariance point which characterizes the composition of the microemulsion. The overall composition of the system of crude oil and injected aqueous surfactant solution will in general be within region III of the diagram.

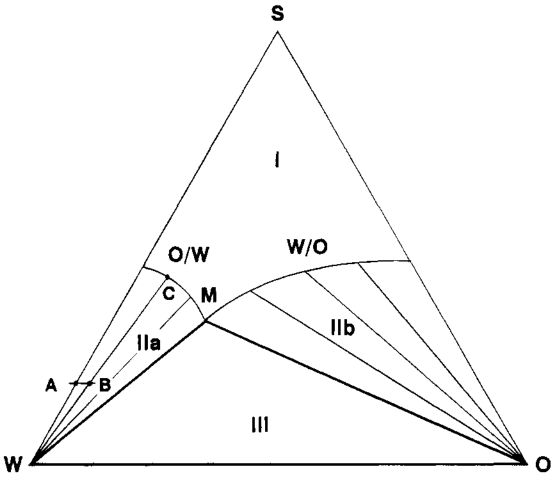


Figure 7. Phase diagram of a system of crude oil (O)/ injected water for the flooding(W)/surfactant (S) forming a microemulsion M at the temperature of the reservoir.

In the process the composition of the surfactant solution injected for flooding is on the WS side, e.g. at point A. This solution is then diluted by water in the pore space so that its composition changes from point A in the direction of W. However, if oil is entrapped in the pore space, the composition changes in the O direction, i.e. it is in the two-phase region, e.g. at point B. This system is then a water phase W and an O/W microemulsion of the composition C. The formation of the microemulsion phase thus indicates residual oil mobilization. If additional oil is solubilized by this two-phase mixture, the microemulsion composition moves along the boundary line CM until point M is reached. If the system flowing within the pore space encounters further oil, the composition is within the region III and three phases are formed, a water phase, an oil phase and an O/W microemulsion of composition M. The single droplets absorbed form an oil bank which can be recovered entirely.

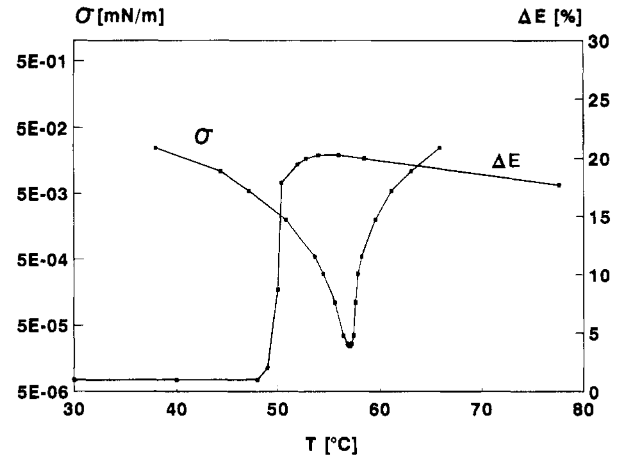


Figure 8. Enhanced oil recovery ΔE in the region of low interfacial tension σ. ΔE is the percentage increase of oil recovery in comparison to the conventional recovery technique.

The correlation between enhanced oil recovery efficiency, ΔE, and extremely low interfacial tension is illustrated in Figure 8.[50] ΔE is that percentage of oil recovered in addition to that amount recovered by conventional techniques. The diagram shows the results of experiments with flooding an oil containing artificial sand bed with surfactant solutions. The interfacial tension between the surfactant solution and the oil decreases with rising temperature. The three-phase region of this system is observed around 57 °C. As soon as σ_{ab} is decreased below 5×10^{-3} mN m^{-1} a steep increase in oil recovery by 20% is observed.

With further increasing temperature the interfacial tension increases again, but no strong decrease in oil recovery is observed. One reason for this higher recovery may be seen in the lower viscosity of the oil at these temperatures. Nevertheless, the complete mechanism is not yet understood, because, not only the interfacial tension between water and oil is of significance for enhanced oil recovery, but also the coalescence of oil ganglions, emulsification processes and interactions with polymers added to the systems in order to adjust the viscosity. This technique of oil recovery has already been studied intensively due to its high economic significance,[4-8] but the variety of interactions still requires numerous investigations before the process is completely understood.The price of crude oil will determine the time when surfactant flooding will be applied in oil recovery. A price of $30 per barrel is estimated to pay the additional costs of the needed surfactants and additives for this technique. Up to that time for every barrel of oil recovered from the reservoir half a barrel is lost in the reservoir. This cannot be recovered later.

B. Liquid–Liquid Extraction

Liquid–liquid extraction is mainly of industrial significance for the extraction of metals from ores with low metal contents. The mineral substances are dissolved in a strongly acidic or strongly alkaline aqueous medium from which they are then recovered by two-phase extraction using a specific extractant.

These extractants are generally large organic molecules which can be dissolved in the oil-rich domains of the microemulsions. The metal ions, on the other hand, are found in the water-rich domains. Since the interfacial area in microemulsions is much larger than in a conventional stirred two-phase system, extraction rates can be achieved exceeding those in conventional two-phase systems by a factor of 10 to 100.[51] A comparison of rates of extraction of Ge(IV) in different microemulsion systems and a conventional system is shown in Figure 9.[52] This technique is in competition with two-phase extractions with LIX (liquid ion exchanger) as extractant, which is applied for example for copper extraction. Because some losses of the surfactant are inevitable, this technique is only suitable for extraction of expensive materials, e.g. rare earth metals.

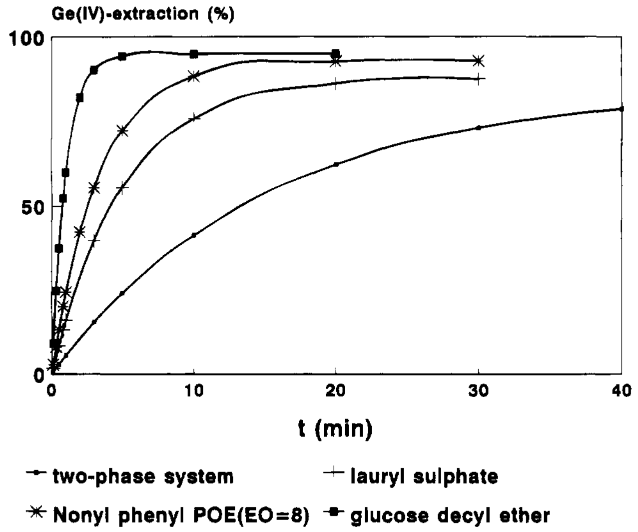


Figure 9. Ge(IV) extraction rates in different microemulsion systems and in a conventional two-phase system.

C. Extraction from Chemically Contaminated Soils

At present, approximately 60% of all soil remediation in Germany is performed by chemicophysical soil washing. In conventional soil washing, organic pollutants are detached from larger soil particles by mechanical energy input.[53] This causes increased adsorption of contaminants at the fine-grain fraction which must then be deposited or burnt. In soil washing with microemulsions, the detached pollutants are solubilized in the oil fraction of the microemulsion as an extractive step in addition to washing. At the same time, the wettability of the soil particles is substantially improved due to the very low interfacial tensions occurring in microemulsions, so that the fine-grain fraction also becomes accessible to washing.

Figure 10 shows experiments concerning the extraction of pyrene, a typical representative of polycyclic aromatic hydrocarbons (PAH), from the fine-grain fraction of a real soil sample using different extraction media. The influence of increasing solubilization capacity of the individual washing solutions on extraction yield can be clearly recognized (determination of the total pyrene content by soxhlet extraction with toluene = 100%). The systems studied are an aqueous solution of $C_{12}E_4$ at a concentration below and above the critical micelle con-

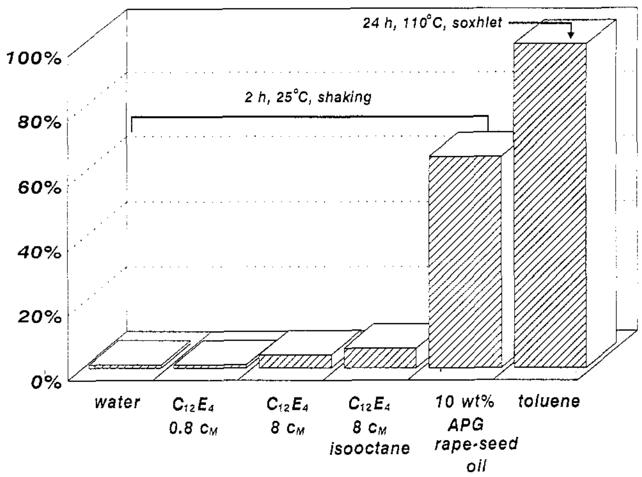


Figure 10. Extraction yields of pyrene from a heavily contaminated fine-grain fraction: influence of the solubilization capacity of the washing solution (total pyrene content determined by soxhlet extraction with toluene). APG = alkyl polyglucoside; c_M = critical micelle concentration.

centration c_M (0.8 c_M and 8 c_M), a ternary mixture of water, $C_{12}E_4$ and isooctane, and a ternary mixture of water alkyl polyglycoside (APG) and rapeseed oil. The latter shows about 70% of the extraction yield compared to pure toluene. The components of this system are chosen to be biodegradable in soil and wastewater. An alternative technique for soil extraction is the application of supercritical CO_2 extraction.[54] This method requires much more expensive equipment. Therefore the extraction method using microemulsions usually offers better facilities.[55]

D. Lubricants and Cutting Oils

These liquids very often contain surfactants and water as additives, i.e. microemulsions or reverse micellar solutions are formed with certain compositions. This has two effects: the surfactants cause corrosion inhibition and the increased water content compared to pure oils leads to higher heat capacity. Corrosion inhibition is based, on the one hand, on solubilization and thus on the inclusion of corrosive agents, which can then no longer react with the metal surface, and, on the other hand, the metal surface is protected by the adsorbed hydrophobic surfactant film. Because of their thermodynamic stability, microemulsion systems have succeeded over instable emulsion systems in this field. The first composition of such a system was patented in 1930.[56] Since that time the systems were improved steadily and are described in numerous patents.

E. Pharmaceuticals and Cosmetics

In the past, emulsions and liquid crystalline systems have been primarily used in the pharmaceutical and cosmetics industry. Compared to conventional organic solvents, these mixtures exhibit higher solubilization capacity. Apart from being generally cheaper, they also permit better stabilization of the pharmaceuticals. In a variety of application microemulsions offer the following general advantages over emulsion systems:[57-60]

(1) The preparation of microemulsions is simple due to thermodynamic stability and therefore cheaper than that of emulsions.

(2) Inhomogeneities and precipitates can be easily detected due to optical transparency and thus avoided.

(3) Storage stability is improved due to the thermodynamic stability of the mixture and the stabilizing effects of the surfactants on pharmaceuticals and cosmetics.

(4) Formulations using microemulsions with suitable protein-compatible surfactants can be used as injection solutions. These formulations can be chosen to be miscible with blood at any ratio.

(5) According to ref 57 microemulsions as solvents do not cause any immunoreactions or fat embolisms, in contrast to emulsions, since the droplet or domain size is considerably smaller and, moreover, can be predefined by the composition. A prerequiste is that components are chosen to be highly biocompatible.

(6) Higher diffusion and skin penetration rates were observed for microemulsions in pharmaceuticals, compared to conventional formulations.

(7) Proteins are not denaturated in microemulsions, since they are localized in the aqueous domains and thus protected against interactions with surfactants and/or oil.

The disadvantages of the microemulsion systems have to be discussed on the background of every single application. There were no general problems described in the papers reviewed here. But for more detailed information we have to refer to special literature.

A very interesting practical example of an application of a microemulsion in the pharmaceutical industry is the solubilization of strongly hydrophobic fluoroalkanes used as short-time blood plasma substitutes to maintain a patient's oxygen supply.[60]

Microemulsion systems can be found which exhibit the above advantages and simultaneously fulfill the following requirements for use in organisms. The components must have a low allergenic potential, exhibit good physiological compatibility, and high biocompatibility. These requirements are fulfilled, for example, by lecithins polysorbates and AOT (sodium bis(2-ethylhexyl)sulfosuccinate).

F. Washing

In addition to conventional liquid detergents, microemulsions can also be used in washing processes. The removal of contaminants from solid surfaces or tissue capillaries is significantly improved by the extremely low interfacial tensions in microemulsion systems. This was also shown quantitatively for the removal of hexadecane from synthetic tissue,[61] which reaches a maximum in the three-phase region of the system, as shown in Figure 11. The effect of cleaning is measured by white light reflectance, expressed as R (%). A maximum of 75% of white light reflectance is about what can be reached with a cleaned tissue.

Nonionic surfactants of the alkyl polyglycol ether group can be used for these formulations, since they exhibit a high washing capacity especially for synthetic tissues and at low washing temperatures. Moreover, ionic surfactants such as dodecyl sulfate (SDS) or hexadecyl sulfate (SHS) can also be used in

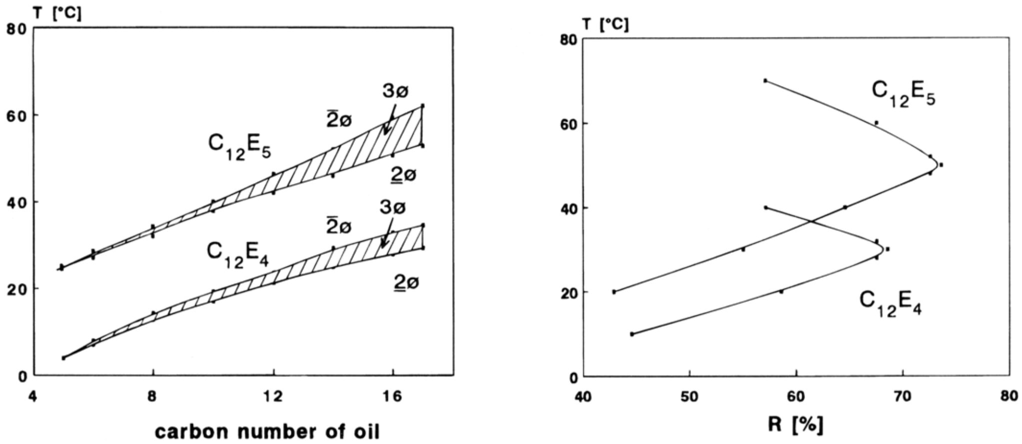


Figure 11. Phase behavior of $C_{12}E_4$ and $C_{12}E_5$ surfactants and cleaning effect: temperature interval of the three-phase region as a function of the chain length of oil (left) and cleaning effect *R* (%) as a function of temperature (right). The cleaning effect is expressed by the percentage of white light reflected by the cleaned textiles.

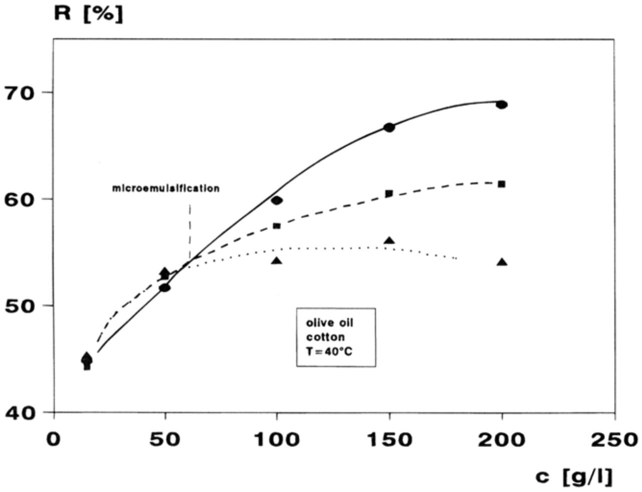


Figure 12. Cleaning effect *R* (%) as a function of the concentration and composition of the wash liquid. SHS = sodium hexadecyl sulfate; LAS = linear alkyl sulfonates. (▲, LAS + nonionic surfactant; ■, liquid detergent; ●, SHS + pentanol.)

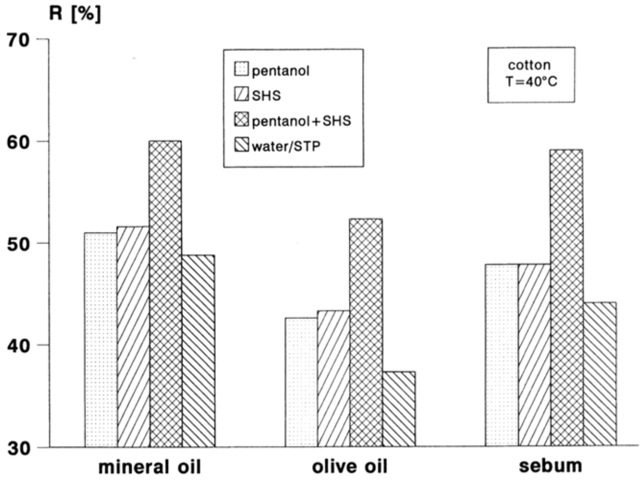


Figure 13. Cleaning effect *R* (%) as a function of the composition of different washing solutions. SHS = sodium hexadecyl sulfate. STP = sodium triphosphate.

combination with cosurfactants such as ethoxylated short-chained aliphatic alcohols. Various additives such as synthetic zeolites improve the properties, e.g. viscosity and secondary washing performance.[62,63]

Microemulsions are often only formed directly during the washing process, and soiling then acts as the nonpolar component, i.e. as the oil fraction in the microemulsion. Figure 12 shows the cleaning effect as a function of composition and concentration of the washing liquid. Soiling was effected by olive oil on cotton and cleaning was carried out at 40 °C. The efficiency of a mixture of linear alkyl sulfonates (LAS) and nonionic surfactants was compared with that of a commercial liquid detergent and a mixture of sodium hexadecyl sulfate (SHS) and pentanol.

It can be seen that the mixture of SHS and pentanol reaches a significantly higher cleaning effect threshold than the other detergents. The difference is especially pronounced at high concentrations, due to the better solubilization of the oil. These high concentrations are usually never reached during washing with liquid or heavy-duty laundry detergents.

The cleaning effect of the mixture of surfactant and cosurfactant is illustrated in Figure 13 by a comparison of the cleaning effect of the individual components for different soilings. A microemulsion which removes the stain can be formed very rapidly only with the system using the combined action of surfactant and cosurfactant. For comparison, *R* (%) is also plotted for water/sodium triphosphate (STP). The advantages of SHS/pentanol over LAS/nonionic surfactants are also illustrated in Figure 14. SHS/pentanol rapidly forms an optically transparent microemulsion, which scatters light only very weakly, whereas LAS/nonionic surfactant forms a turbid dispersion which only cleares very slowly.

A very efficient application of microemulsions in washing processes is therefore the pretreatment of heavily soiled tissue with the surfactant−water mixture forming the microemulsion already during the pretreatment procedure. Detergents can thus be used in a very concentrated form and in selected locations.

Figure 15 compares the cleaning efficiency of several ternary systems with that of commercially available pretreatment systems. The cleaning effect of all ternary systems under investigation composed of ionic and cosurfactants is clearly better for cotton soiled by olive oil than that of commercial detergents. Today usually solvent systems are used for pretreatment. Because of environmental protection these

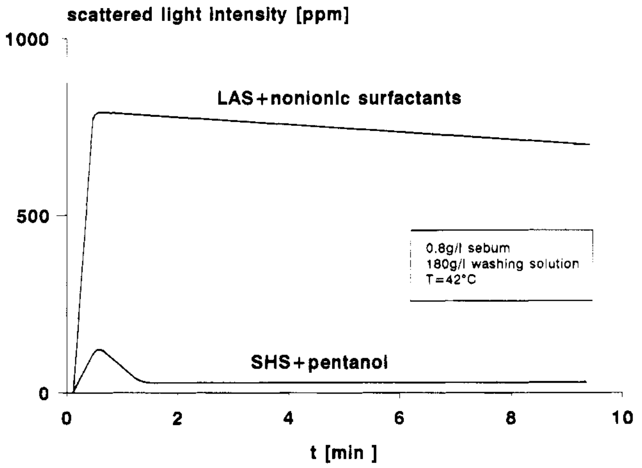


Figure 14. Dissolution of sebum, measured by light scattering, in concentrated wash solutions as a function of time. LAS = linear alkyl sulfonates; SHS = sodium hexadecyl sulfate

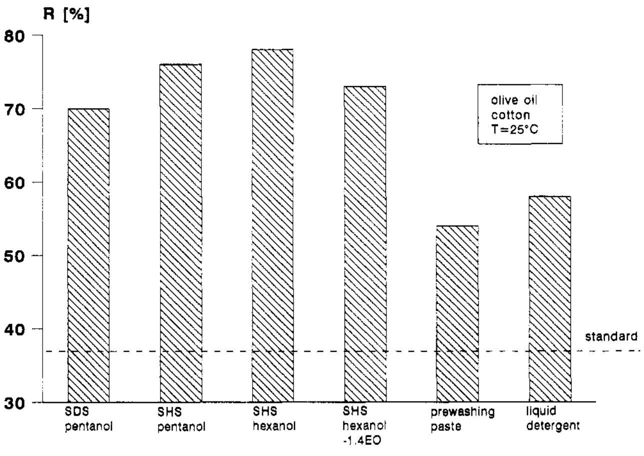


Figure 15. Comparison of the efficiency of different ternary systems and commercial mixtures in textile treatment. SDS = sodium dodecyl sulfate; SHS = sodium hexadecyl sulfate; hexanol−1.4EO = ethoxylated hexanol; 1.4EO = degree of ethoxylation.

systems will no longer be applicable in the future. The surfactant-based systems will replace the former ones.

G. Impregnation and Textile Finishing

Another possible application is the use of microemulsions in textile finishing. Many auxiliary agents used in this field are of an amphiphilic nature. In dyeing, for example, they predominantly have dispersing and retarding functions and act as a fixing agent.

Barni et al.[64] examined the dyeing of nylon-6,6 with an azo dye which reacts with the substrate via an acid−base mechanism. It was shown that the affinity of the dye for the textile fiber is reduced by the use of a microemulsion of Ethofor-DODAB (dioctadecyl dimethyl ammonium bromide)/octanol/water. At the same time, saturation is increased, which is of particular interest for very intensive dyeing. Furthermore, greater homogeneity in dyeing was observed in comparison to conventional dyeing aids. Homogeneity even increases at lower temperatures so that operating temperatures can be reduced and thus energy saved. The relation between the costs for the higher amount of surfactant and the savings or other advantages will decide the success of this application.

Agster[65] describes the preparation of finely dispersed finishes using microemulsions containing siloxane. In comparison with normal emulsion techniques the following advantages were achieved using the microemulsion: higher emulsion stability, excellent product distribution on and in the substrate, pronounced breaking effect, very high internal softness, excellent surface smoothness, increased abrasion resistances and high washing permanence. Water-repellent silicones had to be diluted in organic solvents in the past if they were to be used for outer-wall impregnation and priming or for brickwork drying. When the application of this microemulsion at the wall is finished the silicon is not resoluble in water, because its hydrophilic groups are removed. A new technology now provides solvent-free silicone concentrates which spontaneously form microemulsions with water. The use of water instead of solvents and the concentrate technique contribute effectively to protecting the environment.[66]

H. Chemical Reactions in Microemulsions

Due to the variety in phase equilibria and microstructures these systems were soon of interest to others than basic researchers and petroleum producers. Chemists in all fields of activity studied chemical reactions in these "solutions".[67] In one of the first studies entitled "Catalysis in Water Pools" Menger described in 1973 the accelerated hydrolysis of esters in w/o microemulsions.[68] The aims of many investigations can be divided into two main groups. On the one hand, investigations concerning the physical properties of microemulsions were carried out with the aid of model reactions.[27−32,69−74] For example, it was demonstrated that the water in the aqueous domains exhibits the same physical properties as in a bulk aqueous phase from a diameter of about 2 nm onward. The contents of the water droplets are interchanged on a millisecond time scale. The second major group comprises various experiments aimed at selectively influencing chemical reaction processes by using microemulsions as the reaction medium. A large number of publications are available describing organic, inorganic and biochemical reactions in microemulsions.

1. Nanoparticle Preparation

Microemulsions can be used to produce ultrafine particles with sharp particle size distribution by precipitation. In general, two microemulsions of the same composition, but containing different reactants in the aqueous fraction, are mixed and the precipitate is then isolated. This technique uses an oil−continuous microemulsion in which the water droplets can be regarded as microreactors. The particle size is found to be a function of the size of the water droplets. This is shown, for example, by Robinson et al.[75] in studies of the formation of cadmium sulfide particles in AOT [bis(2-ethylhexyl) sulfosuccinate]/water/*n*-heptane systems. A variation of the water/surfactant ratio shows a correlation between droplet

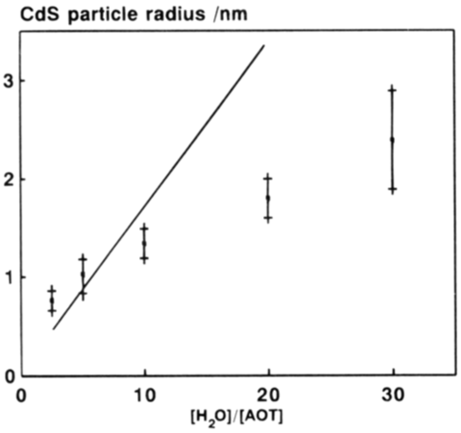


Figure 16. Comparison of particle radius and droplet radius as a function of the composition of the microemulsion. The droplet radius is calculated according to $r = 0.18([H_2O]/[AOT]) + 1.5$ (straight line).

radius (straight line) and particle radius, as shown in Figure 16. But there is no exact 1:1 correlation between the amount of reagent contained in a droplet and that present in a particle formed finally.

The mechanisms of particle formation have not yet been completely clarified, but certain factors of influence can already be specified and general trends described. Osseo-Asare[76] gives a good survey. He describes five aspects to be taken into consideration for particle synthesis in microemulsions: phase behavior and solubilization, average concentration of the reacting species in the aqueous domains, intramicellar interactions, water/surfactant ratio and structure and properties of the solubilizing water, and dynamic behavior of the microemulsion.

The size and position of the microemulsion domain in the phase diagram are significantly influenced by the species solubilized in the reverse micellar phase. An increase in ionic strength generally causes a reduction of the electrostatic interactions between the polar head groups of a surfactant. This leads to a more rigid interface, smaller aggregation numbers, smaller intermicellar forces of attraction, and a reduction in solubilization capacity.

The average number of ions per droplet can be calculated by determining the droplet size in a microemulsion system. It was shown that the distribution follows Poisson's law.[77,78] Nucleation of a solid phase only occurs if a sufficient number of ions is available for forming a stable nucleus. It was demonstrated, for example, for the formation of cadmium sulfide[79] that smaller particles were formed with a high number of ions per droplet as compared to smaller numbers of ions. This is attributable to the higher nucleation rate due to the increased probability of corresponding ions coinciding in one droplet. The nucleation rate, and thus the particle size, can therefore be basically controlled, but it must be taken into consideration that even larger aggregates can be formed after nucleation by agglomeration.

The interactions within a droplet can also decisively influence the particle size. Two factors are responsible for this phenomenon. Firstly, the activity of an ion can be significantly changed in such a

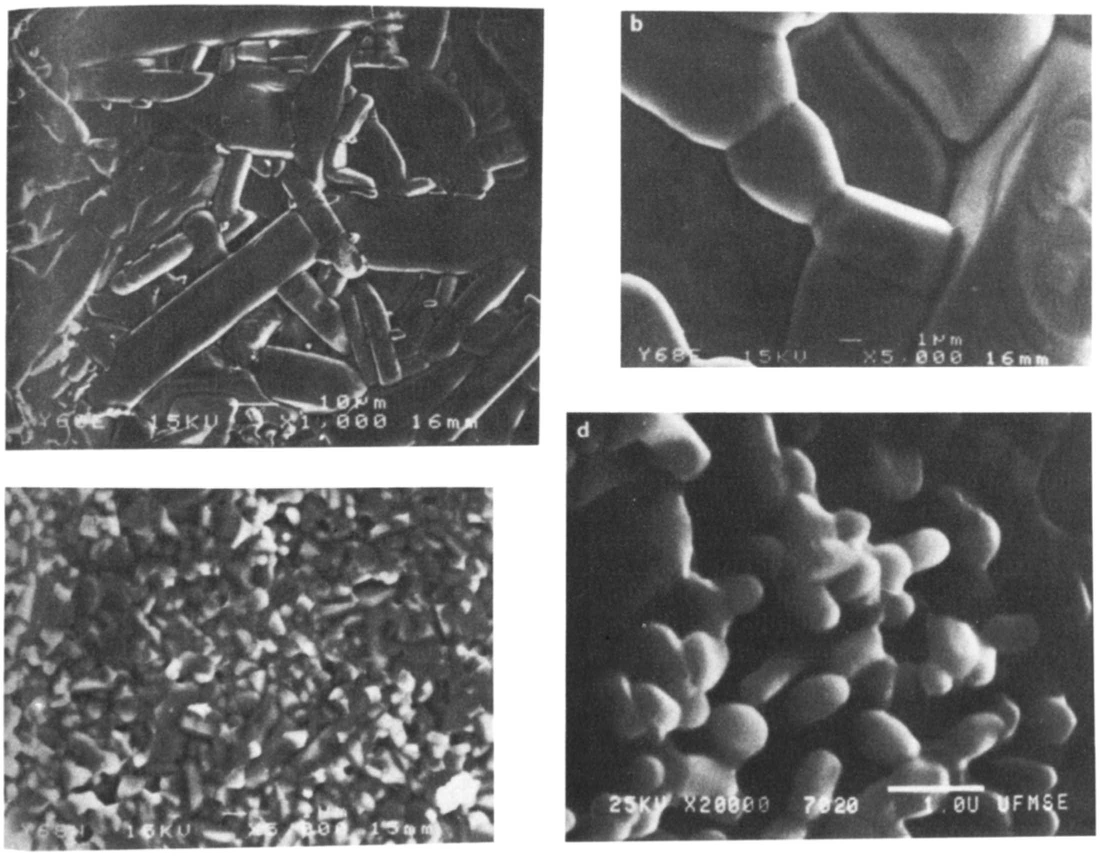


Figure 17. Scanning electron micrographs showing the microstructure of sintered $YBa_2Cu_3O_7$ pellets synthesized by microemulsion-mediated reaction (a,b) and the conventional aqueous reaction (c,d). The magnifications used were (a) 1000, (b) 5000, (c) 5000, (d) 70000.[83]

droplet as compared to a pure aqueous phase and, secondly, the reaction process can be significantly influenced by the localization of a species e.g. at the interface. This effect can be very specific for different ions. Nagy et al.[80] observed, for example, that Fe(III) is strongly hydrated in a water/hexanol/CTAB system and is localized at a distance from the interface, whereas Co(II) ions interact with the hexanol molecules and are therefore preferentially present near the interface. The reaction, and thus the particle size, are also significantly influenced by the concentration of water and surfactant in the microemulsion. In the case of small water/surfactant ratios, most of the water molecules will be bound by solvation of both the surfactant and the reacting species, while the number of "free" water molecules increases in proportion to the W/S ratio. As already discussed, the size of the synthesized particles is also determined by aggregate formation in addition to nucleation. Here the dynamic behavior of the microemulsions is of significance because ion exchange between the domains and the aggregation of nuclei are the decisive processes. Shah[83] performed systematic studies on the precipitation of silver chloride in microemulsions. He found that the coagulation rate of AgCl nuclei increases with the chain length of the oil used and with the amount of cosurfactant, whereas it decreases with increasing chain length of the alcohol.

Particle synthesis in microemulsions is a promising technique, but it has not been possible to date to completely clarify all relevant mechanisms and the synergisms involved. Nevertheless, this technique is tested also in catalyst production, and for semiconductors, photographic suspensions and superconductors.[75,81-88] Figure 17 shows electromicrographs of $YBa_2Cu_3O_7$ superconducting material. Superconductivity critically depends on the microstructure of the material. In this example a material was sythesized by microemulsion precipitation which shows particle sizes by a factor of 10 lower than the smallest particles achievable by bulk solution precipitation.[83]

2. Biochemical Reactions

During his studies with enzymes in nonpolar solvents Martinek found in 1978 that α-chymotrypsin can be solubilized in the water droplets of microemulsions without the activity being lost.[89] This even applies if more than 90 wt % of the microemulsion is a hydrocarbon. These observations by Martinek initiated a great number of studies with various enzymes, which were summarized in reviews by Luisi in 1985 and 1988.[90,91] If hydrophobic substrates are added to the enzyme containing microemulsion, it can be observed that the enzyme-dissolved in the aqueous domains converts the substrate dissolved in hydrocarbon. Enzyme-catalyzed syntheses with water-insoluble substrates in microemulsions can be carried out[93-102] by selecting the components for preparing the microemulsion so that no inhibition or denaturation of the enzyme occurs.[92] An interesting study of an enzyme-catalyzed reaction including enzyme recovery by extraction from the reaction solution is described by Larsson in ref 93. This study shows that reaction control, product isolation, and enzyme recovery from the microemulsion are possible if the phase diagram of the system used is well known.

The isolation of proteins from aqueous solutions by liquid–liquid extraction with a microemulsion can already be regarded as a mature technique.[103] By varying the pH value, ionic strength, or temperature, the distribution coefficient of a protein can be adjusted between a w/o microemulsion and the coexisting aqueous phase so that the protein can be absorbed in or released from the microemulsion.[104,105]

3. Electrochemical and Electrocatalytic Reactions

Electrochemistry often faces the problem of finding a solvent which simultaneously dissolves an organic substrate and a sufficient amount of conducting electrolyte. The use of o/w microemulsions as the reaction medium offers very interesting new possibilities of electrochemical analysis and catalysis.[106-111] The electrochemical synthesis of polyparaphenylenes[111] or the dehalogenation of vicinal dihalogen compounds[109] are interesting new synthesis paths.

4. Polymerizations

The polymerization of styrene and other water-insoluble monomers in microemulsions yields monodisperse latices.[112-117] The microemulsions in which these polymerizations can be carried out contain higher surfactant concentrations than the formulations of technically performed emulsion polymerization. The monodisperse microlatices obtained from microemulsions are in discussion as a seed for emulsion polymerization or as a carrier for pharmaceuticals. Further applications will undoubtedly emerge in the near future. Kaler et al.[118] give a good survey of polymerizations in microemulsions and demonstrate in detail the experimental procedure using the example of styrene polymerization.

5. Organic Reactions

Organic syntheses are often faced with the problem of reacting water-soluble inorganic reactants with water-insoluble organic reactants. It is current practice in these cases to bring the reactants together and thus cause them to react with the aid of polar aprotic solvents, phase transfer catalysts or just by intensive mechanical mixing. Due to the widespread application of phase transfer catalysts these reactions are also referred to as phase transfer reactions. In microemulsions high concentrations of both water-soluble and water-insoluble compounds dissolve simultaneously. This has been recognized in the past 20 years by several groups who used these solutions as reaction media for various organic reactions with reactants such as acids, bases, cyanide, bromide, hypochlorite, or permanganate. Table 1 shows a selection of these activities. In addition to reactions with ionic reactants, experiments were also described concerning the synthesis of macrocyclic lactones,[130,131] the Diels–Alder reaction,[132,133] oxidations with H_2O_2,[134] nitrations of aromatics,[135] as well as catalytic reductions[136] and oxidations[137,138] in microemulsions. In most of the studies described, an already known microemulsion was used as the reaction medium. The reactant concentration was selected just low enough

Table 1. Literature Survey Concerning Organic Reactions in Microemulsions

reaction	amphiphile	concentration (mol/L)	author
acid and alkaline hydrolyses	anionic amphiphile (AOT)	10^{-3} to 10^{-2}	Menger,[68] Mackay,[120] Lamaty,[121]
nucleophilic substitutions: $RX + Y^- \rightarrow RY + X^-$; $Y^- = CN^-, Br^-, R_2CH^-, C_6H_5O^-$	nonionic, anionic, and cationic amphiphiles (C_iE_j, AOT, SDS, CTAB)	10^{-3} to 10^{-2} 4×10^{-2} 10^{-1} 3×10^{-4}	Bunton[122] Jaeger[123] Jursic[124] Schomäcker[74]
oxidations, e.g. of sulfides	nonionic, anionic and cationic amphiphiles	1	Menger,[125] Jursic[126]
oxidations with $KMnO_4$	cationic amphiphiles	10^{-1}	Menger[127]
reductions with $NaBH_4$	nonionic and cationic amphiphiles	10^{-1}	Jaeger,[128] Lattes[129]

to keep the microemulsion stable. So it was only possible to achieve concentrations of up to about 0.1 mol/l, a level that is too low for commercial syntheses. Menger[125] is the only researcher to work with reactant concentrations of about 1 mol/L. This elevated concentration was achieved by compensating the influence of the reactants on the stability of the microemulsion by higher amphiphile concentrations. Menger describes in this paper the oxidation of highly toxic sulfides (mustard oils) with hypochlorites to nontoxic sulfoxides. This work can be a valuable contribution toward solving the problem of the disposal of chemical warfare agents. Menger's example does not include the need for product isolation, but the studies describing organic syntheses do not make any technically feasible proposals in this respect either. The isolation of a reaction product in the presence of the amphiphile poses more problems than an isolation from a simple solvent. It is important to cleave the microemulsion so that product and amphiphile are in two different phases. A study by Jaeger describes the use of an amphiphile in which the hydrophilic head group is connected with the hydrophobic part of the molecule by an acetal bond.[139] After a reaction process in the alkaline region, the amphiphile and thus also the microemulsion can be cleaved by acid addition. Since in this example the amphiphile is lost with every reaction preparation, it is more appropriate to use the knowledge of the phase behavior and achieve phase separation by temperature or pressure variation. Two of our own studies describe how the addition of the reactants changes the phase diagram of the microemulsion. In case no stable microemulsion is obtained at the reaction temperature after adding the reactants, proposals are made on how to change the amphiphile in order to obtain a stable microemulsion for the reaction to proceed with the dissolved reactants at the desired reaction temperature.[140,141] After the reaction process is complete, the microemulsion can be cleaved by changing the temperature and the product can be isolated from the organic or aqueous phase. These studies are based on results of investigations of the phase behavior of microemulsions carried out by the group of M. Kahlweit at the Max Planck Institute for Biophysical Chemistry in Göttingen.[13,14,36] The information on the phase behavior of the microemulsions (described in section I.1) is required in order to use them as the reaction medium for a chemical reaction. The aim is in general to work with maximum possible reactant concentrations in conjunction with minimum possible amphiphile concentrations.

6. Example of a Reaction Process in a Microemulsion

A simple example will be described to show how a microemulsion is used as reaction medium for a phase transfer reaction. Knowledge of the phase behavior is used in order to find the optimum reaction conditions. The process is demonstrated by the example of the hydrolysis of diethyl butyl malonate with aqueous NaOH.

Figure 18 shows a section of the phase prism of the ternary system of water, hexane, and C_8E_5 as the amphiphile. C_8E_5 is the short form for pentaethylene glycol monooctyl ether. At 56 °C a mixture of equal mass fractions of water and hexane forms a microemulsion by the addition of 22 wt % of C_8E_5. The addition of a smaller concentration of C_8E_5 also produces a microemulsion which is in equilibrium with the nonemulsified water and hexane. At a temperature above 62 °C two-phases are observed, the amphiphile being dissolved in the hexane phase. Below 48 °C the mixture exhibits also two-phases,

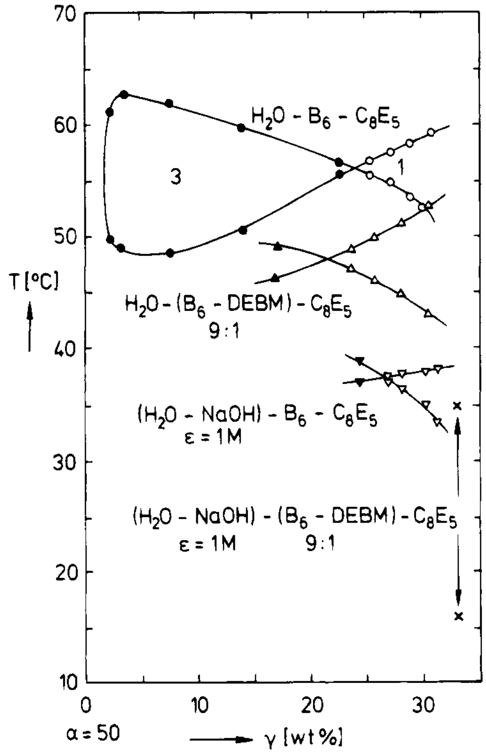


Figure 18. Section of the phase prism for the system of water, hexane, and C_8E_5. The addition of diethyl butylmalonate (DEBM) or NaOH shifts the single-phase region of the mixture toward lower temperatures. A microemulsion of a 10% mixture of DEBM in hexane and 1 molar NaOH has a single-phase stability region from 16 °C to 35 °C.

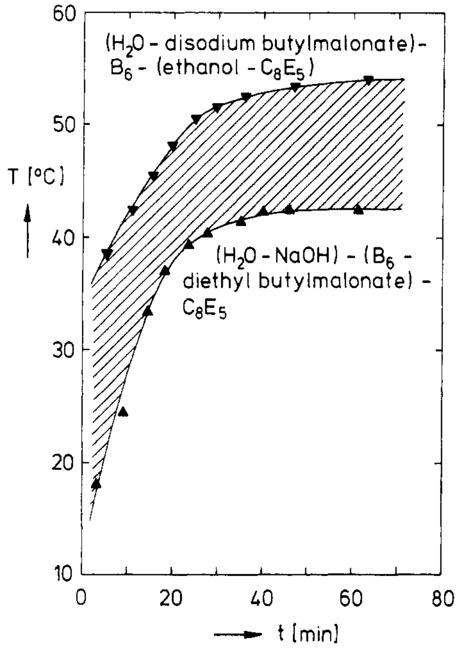


Figure 19. Shift of the single-phase stability region during ester hydrolysis.

but the amphiphile is dissolved in the water phase. If part of the hexane is replaced by diethyl butyl malonate (10%), the stability region of the microemulsion is shifted by approx imately 10 K to lower temperatures. If the water of the ternary mixture is replaced by 1 molar NaOH, the region of stability is shifted by 22 K to lower temperatures. A mixture of a 1 molar NaOH, a 10% mixture of the ester in hexane, and 32 wt % of C_8E_5 forms a single-phase microemulsion between 16 and 35 °C. If this formulation reacts at 25 °C, the microemulsion turns turbid after roughly 10 min. The reaction slows down until, finally, it is interrupted by complete phase separation. A temperature increase produces again a single-phase microemulsion in which the reaction continues. Figure 19 shows how the stability region of the microemulsion is shifted to higher temperatures with proceeding reaction. When the reaction is completed the temperature is increased by approximately 20 K, so that the microemulsion is separated into two phases in which the amphiphile is dissolved in the hexane phase. The reaction product, disodium butylmalonate, can be isolated from the aqueous phase.

In reactions producing an oil-soluble product the isolation occurs after a temperature decrease. For this "demonstration experiment" an amphiphile of medium-chain length was selected. If longer chained amphiphiles are used, such as $C_{12}E_8$, considerably less amphiphile is required for producing a microemulsion (approximately 2–5 wt %), so that such longer chained amphiphiles are preferable in controlled reaction processes. However, it is more difficult to measure the phase diagrams with longer chained amphiphiles because mesophases occur in addition to the phases described. These phases do not play a role for the application of the microemulsion as the reaction medium, they only "complicate the representation" of the results of this demonstration experiment. Reference 141 contains a list of 10 reactions carried out according to the principle described above. They include substitutions, reactions of C–H acidic compounds, hydrolyses, oxidations, and reductions. In all cases, an organic reactant was converted with an ionic reactant. The individual steps of the procedure were in each case:

(1) Selection of an amphiphile forming a microemulsion with the organic reactant and water. If the organic reactant, water, and amphiphile cannot form a microemulsion by themselves, a mixture of the organic reactant with an alkane is used. The phase diagrams for mixtures of alkanes, water, and amphiphiles are well known.[13]

(2) Study of the influence of the inorganic reactants (electrolytes) on the phase behavior of the system. If the stability domain of the microemulsion with the electrolyte deviates excessively from the desired reaction temperature, a more hydrophilic or hydrophobic amphiphile is selected in accordance with Figure 5.

(3) Observation of the influence of the reaction progress on phase behavior. Adapting the temperature to the stability region of the microemulsion.

(4) Phase separation by temperature change after the reaction process. Amphiphile and reaction product should be present in different phases prior to product isolation.

7. Comparison with Phase Transfer Catalysis

The established technique for this type of two-phase reactions is phase transfer catalysis.[142,143] This process involves a two-phase reaction mixture containing one reactant dissolved in the organic and one dissolved in the aqueous phase, to which a quaternary ammonium salt or a crown ether is added as the phase transfer catalyst. This phase transfer catalyst extracts the ionic reactant, e.g. OH^-, CN^-, Br^-, etc., from the aqueous into the organic phase where the ion is present without hydrate shell and is thus very reactive. Figure 20 shows this behavior schematically.

The bottom diagram in Figure 20 schematically shows the reaction mechanism in a microemulsion. Instead of the individual molecules, the aqueous phase in which the reactant is dissolved is transported into the organic phase. The reaction takes place at the internal interface between water and oil. The ions are therefore still present in the hydrated form and are, thus, less reactive than in the case of phase transfer catalysis. This disadvantage is compensated by the significantly larger interface at which the reaction takes place. Kinetic investigations show that, for example, substitution reactions proceed at comparable rates in both systems.[141] This comparison shows that the addition of an arbitrary amphiphile to a two-phase reaction mixture cannot act as efficiently as a phase transfer catalyst. The reaction can only be effectively accelerated by an amphiphile dispersing the organic and the aqueous phase as a microemulsion. Both methods, phase transfer catalysis and reaction in a microemulsion, have benefits and disadvantages. Designing a reaction in a microemulsion is more sophisticated than using a phase transfer catalyst. For a laboratory-scale synthesis the expenditure for determining the phase diagrams is generally too high. This expen-

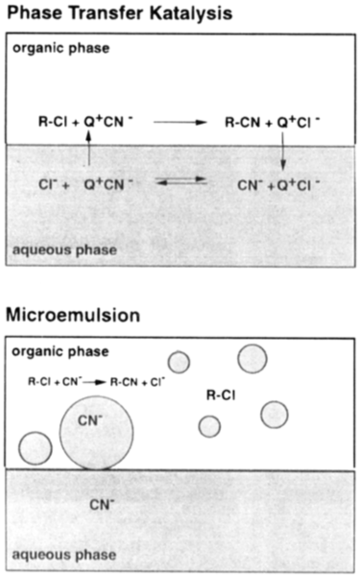


Figure 20. Mechanism of a reaction process with phase transfer catalysis and in a microemulsion.

diture is only meaningful for reactions repeated frequently and on a large scale. The quaternary ammonium salts used as phase transfer catalysts are strong fish poisons, and their application in reaction processes on a technical scale is often avoided since they could be passed into the wastewater. Nonionic amphiphiles do not present any hazard under the aspect of environmental compatibility because they are completely degraded in sewage plants. Since the environmental compatibility of a chemical process plays an ever increasing role, microemulsions may become an interesting alternative to the use of toxic polar organic solvents or phase transfer catalysts. In the author's laboratory, the process engineering aspects of the use of microemulsions as reaction media are therefore currently being studied. In addition to the selection of reactions suitable for operation with a microemulsion as the reaction medium, work is centered on issues of product isolation using the systems' phase behavior and on amphiphile recovery for reuse.

IV. Summary

The large variety of applications as well as the steadily increasing number of working groups engaged in studies on microemulsions already show their present significance for many branches of chemistry and suggest that microemulsions will become even more significant in the future. We hope to have given an insight into this wide field of activities and possibly also to have made some suggestions which may be of use for the reader.

V. References

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