

Microemulsions

Background, New Concepts,
Applications, Perspectives

Edited by
Cosima Stubenrauch



 WILEY

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School of Chemical and Bioprocess Engineering,
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A John Wiley and Sons, Ltd, Publication

This edition first published 2009
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Blackwell Publishing was acquired by John Wiley & Sons in February 2007. Blackwell's publishing programme has been merged with Wiley's global Scientific, Technical, and Medical business to form Wiley-Blackwell.

Registered office

John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

Editorial offices

9600 Garsington Road, Oxford, OX4 2DQ, United Kingdom
2121 State Avenue, Ames, Iowa 50014-8300, USA

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Library of Congress Cataloging-in-Publication Data

Microemulsions : background, new concepts, applications, perspectives/edited
by Cosima Stubenrauch. – 1st ed.

p. cm

Includes bibliographical references and index.

ISBN 978-1-4051-6782-6 (hardback : alk. paper)

1. Emulsions. I. Stubenrauch, Cosima.

TP156.E6M5175 2008

660'.294514--dc22

2008013076

A catalogue record for this book is available from the British Library.

Set in 10/12 pt Minion by Aptara Inc., New Delhi, India
Printed in Singapore by Markono Print Media Pte Ltd

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Chapter 10

Microemulsions in Large-Scale Applications

*Franz-Hubert Haegel, Juan Carlos Lopez,
Jean-Louis Salager and Sandra Engelskirchen*

10.1 Introduction

10.1.1 General considerations

The unique properties of microemulsions make them interesting for commercial products and technical processes [1]. In particular, the high solubilising power of microemulsions and microemulsion systems for organic and inorganic compounds favours their use as solvents for a large number of applications. However, cost arguments and the complex behaviour of multicomponent systems forming microemulsion phases have been obstacles to large-scale applications in the past. But the increasing number of patents beginning in the 1990s now shows that many problems could be solved with systematic studies on the structure [2] and the phase behaviour of microemulsions [3, 4]. Increasing knowledge of multiphase systems comprising microemulsion phases led to tailor-made microemulsions, e.g. with enhanced temperature stability [5], low surfactant content [6] and diverse polar oils from natural [7–9] or petrochemical sources [10, 11]. Concentrates have been developed which can be diluted without phase separation thus forming kinetically stable emulsions or even remaining microemulsions over the whole concentration range [12, 13]. Effective surfactants and surfactant mixtures have been found enabling the formation of microemulsions with various oils [14, 15].

Meanwhile, there are a variety of large-scale applications of microemulsion systems. Many products used in daily life contain microemulsions or formulations which are able to form microemulsions (some prominent examples are discussed in Chapters 8 and 9 of this book). Concentrates, surfactants or surfactant mixtures which can be used for microemulsification are frequently applied. All these materials are produced and handled in large quantities. In particular, oil-in-water (o/w) droplet and water-in-oil (w/o) droplet microemulsions are found in many products or technical processes today. Whereas their usage is not very different from ordinary solvents in most cases, the use of bicontinuous microemulsions poses specific problems which will be discussed later on.

10.1.2 Products and processes

O/w-droplet microemulsions are widespread in cleaners, cosmetics and personal care products (see Chapter 8). They are also used as solvents for pharmaceuticals (see Chapter 9) and agrochemicals [16]. In particular, pharmaceutically active ingredients [17] and pesticides [18] which are poorly soluble or insoluble in water can be readily dissolved in o/w-droplet microemulsions. O/w-droplet microemulsions are also used as carriers for biocides in wood preservation [19]. W/o-droplet microemulsions can be found in fuels (see Chapter 11), but also in more sensitive products like cosmetics (see Chapter 8) and food [20, 21]. They can also be used as media for enzymatic reactions.

For a long time, bicontinuous microemulsions were considered to be less suitable for use in products of daily life owing to the limited thermal stability of the single phase. For application in technical processes, however, this problem is often less important. Optimised surfactant systems can in many cases increase the thermal stability to a sufficiently large temperature range for this purpose. Cost arguments connected with the relatively high content of surfactants can often be overcome now by very efficient surfactant systems with polymeric boosters [22]. In technical processes, the application of bicontinuous microemulsions or multiphase microemulsion systems containing a bicontinuous phase already plays an important role. Thus, for example, the production of emulsions can be improved by using bicontinuous microemulsions as intermediates [23]. The temperature dependence of two-phase microemulsion systems can be used for fast and effective separation processes. Extraction of metals [24, 25], dyes [26] and pollutants [27] are examples for improving production processes and reducing environmental problems. However, products containing bicontinuous microemulsions are also commercially available. They are used in cleaning processes, in particular. If conventional detergents are not efficient enough and organic solvents are used instead, bicontinuous microemulsions can often be preferably applied for cleaning. One of the most prominent examples is the removal of ink [28, 29]. Bicontinuous microemulsions can also be used for decontamination of chemical and biological warfare agents [30]. They are further applied for various technical processes, e.g. in textile finishing [31].

All types of microemulsions are also suitable solvents for synthetic processes (see Chapter 5). Fluoropolymer dispersions can favourably be made in microemulsions [32]. In synthetic processes which yield a solid, the structure of the microemulsion can strongly influence the structure and properties of the product [33, 34]. Conductive polymers can be obtained by using o/w-droplet microemulsions of the monomers [35], but it is also possible to increase the content of monomers into the bicontinuous concentration range [36]. The large-scale application of microemulsions in further emerging technologies can be expected. The synthesis of nanoparticles with w/o-droplet microemulsions as hydrolysing agents for metal alkoxides or other strongly reactive precursors is an important example (see Chapter 6 and [37]). It yields products of excellent properties suitable for further improving high-tech commercial products in electroceramics [38]. Patents on microemulsions can also be found for many other applications, e.g. for lubrication in metal processing, corrosion inhibition and protection of buildings from humidity.

In this chapter, three applications at different stages of development will be presented in detail. Whereas the application in soil decontamination is still in the experimental phase,

leather degreasing is already an applied technology and enhanced oil recovery (EOR) is one of the oldest large-scale applications of microemulsion systems.

10.1.3 Requirements for large-scale applications

For large-scale applications, microemulsions have often to fulfil further requirements which are not directly connected to the desired phase behaviour or the structure. Harmlessness, biocompatibility, biodegradability or long-term stability of all components may be needed depending on the application. Inertness and tolerance to the contacted target materials is necessary. Last but not least, cost-effectiveness of the components also plays a very important role.

If large quantities are used for technical processes, e.g. for cleaning, the recovery and reuse of the microemulsion or at least of a considerable amount of the most expensive components is desired. Therefore, strategies are needed to separate contaminants from the organic microemulsion components. Separation is usually more complicated than from ordinary solvents and often requires several steps [39, 40]. In particular, the separation of waste materials from the surfactants is usually very difficult or often even impossible. The temperature-dependent phase behaviour of bicontinuous microemulsions, however, can sometimes be beneficially used for separation [41]. Easy separation, at least from the unpolar solvent, can be achieved from microemulsions with supercritical liquids [42].

Other problems connected with large-scale applications are due to the fact that technical or natural materials have to be used. The composition of natural and technical products, which are often made from natural materials, is not exactly the same for different loads. Thus, the phase boundaries can be more or less changed. Technical non-ionic surfactants generally show skewed fish diagrams (see Fig. 1.8 in Chapter 1) due to the presence of surface-active species of different hydrophilicity. Non-ionic surfactants with the same formal degree of ethoxylation may exhibit different behaviour depending on the actual distribution of molecular weight. In particular, the amount of unreacted alcohol has a significant influence on the phase boundaries. As a consequence, quality control of the components used for microemulsion formation is very important.

Whereas the preparation of microemulsions is usually a very simple process on the laboratory scale, some important aspects have to be kept in mind when making large quantities of microemulsions. Weighing the components is very exact and easy for masses up to 100 kg, but less practicable for larger scales. Dosing by volume, however, is considerably less exact and requires good equipment and the strict exclusion of errors. These requirements can usually be fulfilled only in technical plants. If the composition of a microemulsion must be very exact, on-line control of known parameters, like electrical conductivity, turbidity, viscosity or ion activity, with strict temperature control may be helpful. Another important aspect which can be crucial for the preparation and handling of large quantities of microemulsions is the intermediate formation of liquid crystals. This must be avoided by all means because liquid crystals need a long time to dissolve, even when the temperature is raised considerably above the phase boundary of the liquid crystal. Usually, the formation of liquid crystals can be avoided during preparation if the components are added in a certain order. In most cases water should be added as the last component because it is the component with the highest structuring effect.

Depending on the application, the microemulsions or preconcentrates must be sufficiently thermally and chemically stable. Easy handling is often required over a wide range of temperatures. Whereas for short-term applications within a technical plant, these needs can usually be fulfilled, application elsewhere including transport and long-term storage may require further efforts. Phase separation and liquid crystal formation, in particular, as well as chemical or photochemical reactions of components during transport and storage may cause serious problems when working with large quantities of microemulsions.

10.2 Soil decontamination

10.2.1 Requirements

The task seems to be very similar to EOR, namely extracting an organic liquid from a porous medium and separating it from the aqueous phase, but actually there are decisive differences. First of all, the temperature is different. Whereas elevated temperatures are found in oil reservoirs, the temperature of water in an aquifer is usually between 8 and 16°C. Therefore, other surfactants are required for in situ soil remediation. The problem of liquid crystal formation increases dramatically with decreasing temperature. At any rate, the viscosity of the microemulsion is increased. Large pressure gradients, which can be used in rock formations for transporting the liquid, cannot be applied in soil. Since parts of the microemulsions or surfactants will remain in the soil, the components must exhibit sufficient biodegradability. They must not be hazardous for the groundwater. The properties of some organic liquid contaminants are very different from crude oil. The polarity of aromatic hydrocarbons or chlorinated hydrocarbons is much larger and usual surfactants are not sufficiently effective for these contaminants. The extraction of 80% of the organic liquid would be a remarkable result for oil recovery, but hardly sufficient for a remediation process. The recovery of surfactants and other components and their reuse also require higher efficiency of the separation processes.

Even if some large-scale experiments on soil decontamination have already been performed, the application of microemulsion technology for this purpose is still largely a matter of research. Surfactants have often been applied in field-scale experiments or even commercial cases for the mobilisation and solubilisation of organic pollutants. However, the state-of-the-art of surfactant-enhanced subsurface and aquifer remediation is very different depending on the type of contaminant, the actual situation of the contamination, and the processes used for decontamination. Mobilisation of liquid phases can be, but need not be, connected with the formation of microemulsions. This process is favoured by the very low interfacial tension between the flushing solution and the liquid contaminant, as achieved for Winsor III systems, i.e. those which form a middle-phase microemulsion (bicontinuous microemulsion). If solubilisation is involved, swollen micelles or microemulsions are formed during extraction of liquid contaminants from soil. Since there is often no exact boundary between micellar or interfacial processes and microemulsification, many field-scale experiments might fall within the scope of this contribution. However, only a selection of activities involving the development of very effective surfactant systems for the microemulsification of liquid contaminants and the use of preformed microemulsions will be considered here.

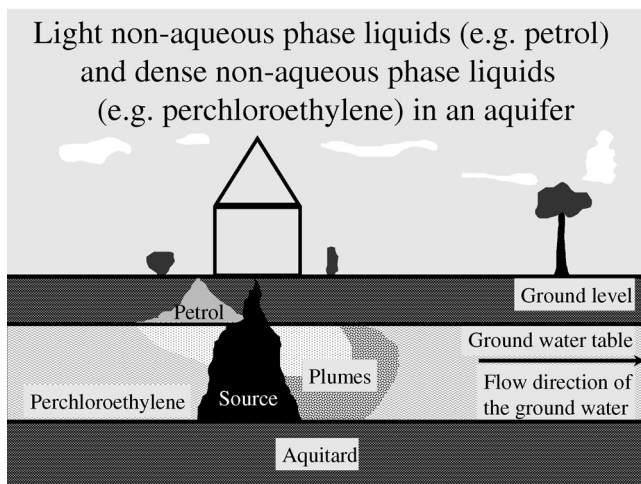


Figure 10.1 Sources and plumes of light non-aqueous phase liquids (LNAPL) and dense non-aqueous phase liquids (DNAPL) in an aquifer. DNAPL can penetrate the ground water table.

10.2.2 Non-aqueous phase liquids

Surfactants and microemulsion systems can be used for ex situ treatment of contaminated soil or in situ soil decontamination. In situ remediation is usually preferred if excavation of the contaminated soil is not possible or expensive, e.g. beneath buildings or for contaminations at great depth. Often bioremediation or natural attenuation is used for decontamination. In most cases, these techniques only permit the effective degradation of contaminants in the plume formed by dissolved pollutants which may be very large. However, for the remediation of a contaminated site, it is also necessary to remove the source where the pollutants may be adsorbed in large quantities or may be present as solid or liquid phases. The latter are called NAPL (non-aqueous phase liquids) and a differentiation is made between LNAPL (light non-aqueous phase liquids) with a lower density than water and DNAPL (dense non-aqueous phase liquids) with a higher density than water (see Fig. 10.1).

The choice of suitable surfactants and additional chemicals for the decontamination of source zones largely depends on the type of pollutant and the structure of the soil (mainly on adsorption behaviour and hydraulic conductivity). Adsorbed and solid pollutants or very viscous liquid phases cannot be mobilised. Preformed microemulsions, co-solvents or co-surfactants can be favourably used for such contaminations in order to enhance the solubilisation capacity of surfactants. NAPL with low viscosity can easily be mobilised and also effectively solubilised by microemulsion-forming surfactant systems. Mobilisation is usually much more efficient. It is achieved by reducing the interfacial tension between NAPL and water. Droplets of organic liquids, which are trapped in the pore bodies, can more easily be transported through the pore necks at lower interfacial tension (see Fig. 10.2). The onset of mobilisation is determined by the trapping number, which is dependent on

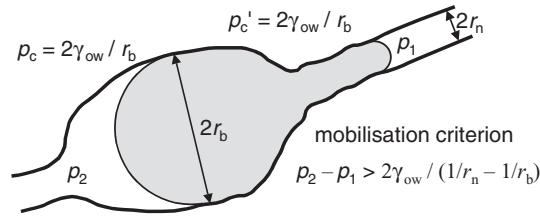


Figure 10.2 Mobilisation criterion for an NAPL droplet trapped in a pore. Pressure difference $p_2 - p_1$ must exceed the difference of capillary pressure $p'_c - p_c$. γ_{ow} = interfacial tension NAPL/water, r_b = radius of pore body, r_n = radius of the pore neck.

soil structure (absolute and relative size of pore bodies and pore necks), flow conditions, density of the contaminant and interfacial tension [43].

Efficient in situ techniques are urgently needed, in particular for DNAPL site remediation [44]. This type of contamination is the most serious and widespread. Many of the sites contaminated with chlorinated hydrocarbons are found in built-up areas, e.g. beneath (disused) dry-cleaning facilities or metal processing plants. DNAPL contamination is very frequent and is often found at great depth beneath the groundwater table in the saturated zone of an aquifer. The pollutant is often concentrated in pools and not, or at least not sufficiently biodegradable, in this position. Microemulsion techniques seem to be most efficient for in situ remediation of DNAPL sources. They may also be interesting for LNAPL sites where the pollutant is less volatile or found in part in the saturated zone owing to fluctuations of the groundwater table.

10.2.3 Microemulsion-forming systems

10.2.3.1 Early research

The findings of early research on surfactant-enhanced aquifer remediation and microemulsification of contaminants, which was strongly influenced by studies on EOR, has been summarised by Harwell *et al.* [45]. In their paper, they also discuss some of the problems related to surfactant injection into the subsurface. First of all, the need for research on biodegradation under aquifer conditions is emphasised. The low temperature and the formation of liquid crystals or gels have also been considered. The measures to obviate liquid crystals or gels are critically discussed. Addition of lower alcohols as co-solvents or co-surfactants implies the use of volatile flammable liquids, which have a considerable potential for contaminating the groundwater and which make the separation and recovery of the active components difficult. Application of branched surfactants, which usually effectively suppress the formation of liquid crystals [46–48], may cause problems owing to their reduced biodegradability [49].

At that time, some large-scale field tests on surfactant and microemulsion technologies had already been performed [50–55]. In most cases, the applied surfactants or microemulsion components were selected in laboratory experiments by determining phase behaviour, interfacial tension, solubilisation capacity, viscosity and extracting power in soil columns.

The expertise with EOR was used for finding suitable microemulsion-forming systems for LNAPL. However, the high polarity of chlorinated hydrocarbons with very low or even negative equivalent alkane carbon numbers (EACN) required novel types of surfactants [56]. The enhanced solubility of surfactants in the oil phase makes most surfactants less effective for solubilisation. DNAPL extraction by mobilisation, however, is problematic owing to the high density of the pollutants, since they may be displaced into deeper soil compartments [57]. This probably happened in at least one field test [58].

Mobilisation of NAPL generally leads to the formation of an oil bank (see Chapter 10.3) in front of the surfactant solution. If the solubilisation capacity of the surfactant solution is too low, large amounts of emulsions will be formed, which can clog the pore space. As the flow in columns is forced, these experiments may not correctly reflect the behaviour of the multiphase system under free flowing conditions in a three-dimensional pore space.

10.2.3.2 *Microemulsion-forming surfactants for chlorinated hydrocarbons*

All types of microemulsions were obtained in salinity scans with mixtures of Aerosol MA (sodium dihexyl sulphosuccinate) and twin-tailed (Guerbet and Exxon type) alcohol ethoxy and propoxy sulphates for perchloroethylene (PCE), carbon tetrachloride, 1,2-dichlorobenzene and trichloroethylene [59] at 25°C. At lower temperatures, however, stable macroemulsions are formed. Chloroform, 1,2-dichloroethane and other chlorinated hydrocarbons were found to be too polar for those anionic surfactants. Extremely hydrophilic and temperature-insensitive surfactants are necessary for effective solubilisation of chlorinated hydrocarbons yielding Winsor III systems. *N*-methyl-*N*-*D*-glucalkaneamide surfactants showed good performance for DNAPL solubilisation even at 16°C [56].

All the systems described thus far require relatively high salinity, which is considered to be critical in soil remediation processes [60]. Another approach for effective microemulsification of organic liquids is the use of co-surfactants. Sodium mono- and dimethyl naphthalene sulphonate were found to be effective co-surfactants in formulations with Aerosol OT (sodium bis(2-ethylhexyl) sulphosuccinate) for diverse chlorinated hydrocarbons and their mixtures between 15 and 25°C [60, 61]. All types of microemulsions could be obtained with this approach.

10.2.3.3 *DNAPL remediation*

As there are other less sophisticated and less expensive techniques available, surfactant-enhanced aquifer remediation will only be useful for decontamination of LNAPL sites in special cases. However, applicable techniques are still needed for DNAPL sites and microemulsion techniques are really promising. Therefore, most research has concentrated on this type of contaminant in recent years. Integrated concepts have been developed including aspects of soil properties [47, 48, 62, 63], density control [47, 48, 62–64], recovery and reuse of microemulsion components [47], biological degradation of residues of contaminants and injected compounds [48, 65] and costs [47, 48, 64, 65]. Two main approaches have been followed for developing effective surfactant systems which form microemulsions with DNAPL, but do not mobilise the liquid contaminant into deeper

aquifer compartments. One approach is based on optimising the solubilisation capacity without reducing the interfacial tension below a critical level [47], and the second is a concept based on neutral buoyancy [66, 67] by the addition of co-solvents which might be injected in the form of emulsions or aqueous solutions followed by surfactant flushing [68]. A third approach to obviate downward migration of DNAPL is the use of concentrated salt solutions injected beneath the DNAPL [69].

10.2.3.4 *Supersolubilisation*

Whereas Winsor III systems exhibit ultra-low interfacial tensions between the three phases and also very high solubilisation capacity, Winsor I systems have higher interfacial tensions and much lower solubilising power. At the transition between the two types of microemulsion systems, an intermediate behaviour can be found which is called supersolubilisation [47, 70]. The uptake of oils into surfactant aggregates is usually enhanced by one to two orders of magnitude compared to effective micellar systems, but interfacial tension reduction is still moderate. The transition point can be adjusted by varying the salinity or organic components.

Supersolubilisation of NAPL can be achieved by adding lipophilic linkers to the system. Best results for chlorinated hydrocarbons were obtained with both hydrophilic and lipophilic linkers [71]. Lipophilic linkers increase the interaction between surfactant and oil [72], and hydrophilic linkers the interaction between surfactant and water. Systems with Aerosol MA as surfactant, sodium mono- and dimethyl naphthalate as hydrophilic linker, and dodecanol as lipophilic linker display the best performance regarding efficiency, economy and environmental aspects [65].

In order to use supersolubilisation for DNAPL extraction, the reduction of interfacial tension must be well controlled. The critical level of interfacial tension is dependent on size and heterogeneity of the pore space. For example, a value of 4 mN m^{-1} was found for soil from a contaminated site [47]. Since supersolubilising systems exhibit lower interfacial tension, they cannot be directly applied for contaminant extraction. Therefore, a salinity gradient was used for column experiments in preparation for a field test [47, 63]. When the salinity was increased in two steps from 0 to 0.6 wt.% and 1 wt.% CaCl_2 , a mixture of a sulphated alkyl propoxylate (Isalchem 145-4PO-SO₄) and a twin-head aromatic sulphonate (Dowfax 8390) exhibited the usual micellar solubilisation, supersolubilisation and formation of bicontinuous microemulsions with perchloroethylene. Applying this three-step gradient to soil columns contaminated with PCE yielded high extraction values and no mobilisation of DNAPL [47].

10.2.3.5 *Concept of neutral buoyancy*

DNAPL extraction without vertical displacement of the contaminant can also be achieved by adjusting the density of the microemulsion which is formed in the subsurface to the density of water by the addition of organic components with densities of considerably less than 1 g/cm^3 . Co-solvents, co-surfactants and some non-ionic surfactants can be considered for this purpose. Whereas the addition of isopropyl alcohol as co-solvent to the surfactant was successful [48, 62, 73], an attempt with pentanol as co-surfactant was not successful, because partitioning of the co-surfactant into perchloroethylene was

too great [73]. A mixture of 5% Aerosol MA-80 (4% active branched sodium dihexyl sulphosuccinate) and up to 8% isopropyl alcohol in 0.6% aqueous NaCl solution was used for the experiments. Furthermore, xanthan gum was added to the surfactant system in order to enhance the viscosity, increase the forces exerted by flow and prevent fingering [64]. Optimum conditions for surfactant-enhanced aquifer remediation at neutral buoyancy were calculated for a medium-scale laboratory experiment from scaling groups regarding the pore structure and the properties of contaminant and surfactant mixture [74].

10.2.3.6 Large-scale experiments

References to large-scale surfactant-enhanced aquifer remediation can be found in the literature [75, 76]. Childs *et al.* also report results from the test site at Dover Air Force Base, Delaware [76]. Large data sets are also available from field tests at Hill Air Force Base, Utah [47, 77, 78]. Other field tests were performed at the Canadian Forces Base, Borden [51, 53], Ontario, the Bachman Road site at Oscoda [79, 80], Michigan, as well as Camp Lejeune, North Carolina [81], Traverse City Coast Guard Base, Michigan [54], Spartan Chemical Company Superfund Site, Michigan [82] and the former Naval Air Station Alameda, California [82, 83]. In the latter case a 97% extraction of DNAPL is reported [83].

10.2.4 Use of preformed microemulsions

Preformed microemulsions can also be used for soil decontamination. The application of bioremediation with microemulsions containing nutrients for oil spills is already a well-known technology [84, 85] and is also proposed for in situ treatment of DNAPL sites [86]. Studies on contaminant extraction, however, are less frequent. In most cases, these systems have been discussed and investigated for adsorbed or highly viscous contaminants which can only be solubilised. Enhancement of solubilisation in microemulsions compared with surfactant solutions was found for pyrene [87] and patented for ex situ treatment of contaminated soil [88]. An interesting cost-effective variation uses partially sulphated castor oil [89].

W/o-droplet microemulsions with non-ionic surfactants containing rapeseed oil methyl ester have been successfully used for in situ extraction of polycyclic aromatic hydrocarbons [40]. However, enhancement of oil content and solubilisation capacity failed with these systems. The use of co-surfactants and co-solvents for suppression of liquid crystal formation was considered to be critical for in situ application.

A complex system containing a branched anionic surfactant, non-ionic surfactants, rapeseed oil methyl ester and an aqueous calcium chloride solution was found to form bicontinuous microemulsions even at low temperatures [46, 90]. This type of microemulsion has been studied for DNAPL extraction on a large scale in an artificial aquifer and later in a joint project with different partners financed by the German Federal Ministry of Education and Research (BMBF) [91]. The project network applied an integrated concept regarding aspects of hydraulics, reuse and biodegradation [92]. Three large-scale experiments each with some hundreds of litres of preformed microemulsion were performed. Whereas extraction of perchloroethylene in the field-scale experiment was not successful

owing to an insufficient quantity of microemulsion and the lack of a focussing extraction well, a later test in a large container removed nearly all the perchloroethylene [91]. Biodegradation of the microemulsion components was achieved under field conditions. Even the biodegradation of sodium bis(2-ethylhexyl) sulphosuccinate, which was known only for liquid cultures from the literature [93], was proven under aquifer conditions [91]. Moreover, dehalogenation of perchlorethylene was found after microemulsion application, such as after surfactant flushing at other field sites [80].

Preformed microemulsions containing co-solvents and co-surfactants have been used for laboratory experiments [94] and a field test [55] in Canada. The systems were developed for the extraction of a viscous oil containing up to 16% of chlorinated solvents from a site at Ville Mercier. The contaminant is a DNAPL with a density of 1.05 g/cm³ and thus exhibits only a small density difference compared to chlorinated solvents [94]. It could not be extracted effectively by the usual Winsor I systems containing *n*-butanol as a co-surfactant. The addition of solvents was necessary for effective solubilisation of the contaminant [94]. A preformed microemulsion containing *D*-limonene, toluene, *n*-butanol, Hostapur SAS (secondary alkane sulphonate sodium salt) and water was injected into a field test site at Thouin Sand Pit near Montreal. In previous column experiments, a composition of 13.16% *D*-limonene, 13.16% toluene, 9.21% *n*-butanol, 9.21% Hostapur SAS and 0.3% of sodium ortho-silicate in water was used as a preformed microemulsion for the extraction of DNAPL from Ville Mercier.

10.2.5 Challenges

Applying the microemulsion technology on a large scale at contaminated sites may sometimes cause surprising problems. Thus, the formation of emulsions, gels or liquid crystals, or the mobilisation of fine soil particles may clog the aquifer. Since soil and contaminant distribution are usually very heterogeneous, these problems may not have been found in laboratory experiments. Additional chemical compounds in the soil can induce such problems [75]. Other problems are concerned with the processing of injected systems and effluents. Safety measures will be needed if highly volatile liquids like low alcohols are used. The BMBF project network already encountered some problems when preparing the microemulsion. Natural products like rapeseed oil methyl ester exhibit different solubilisation behaviour depending on the region, the growing conditions and the process of refinement. Slight differences were found for samples of different origins. At this point, the formation of liquid crystals was found for one sample at room temperature. When all samples were checked, a massive presence of liquid crystals at lower temperature was found for a formulation which some time before had worked very well. Intensive research identified the anionic surfactant as the problematic compound. The producer had changed the formulation slightly. Thus, the phase behaviour had to be studied once again. But not only oil and surfactants can cause problems, even the salt (CaCl₂ · 2H₂O) used at the field site did not have the exact composition as was found by analysing the microemulsion. The use of technical products may sometimes cause problems for microemulsion formation, which may be very sensitive to slight changes.

Surfactant-enhanced aquifer remediation is relatively expensive. Thus, waste reduction or the reuse of at least a considerable part of the microemulsion components is interesting.

Depending on the technology applied and the contaminant, different technologies have been studied for separating the pollutant from the components of the flushing solutions. Simple methods aim at waste reduction, i.e. separation of the contaminant and the surfactant from waste water. Addition of NaCl at elevated temperatures to a field-generated microemulsion of Winsor type I from a field test at Hill Air Force Base, Utah, and centrifugation were used to reduce the volume of the highly contaminated waste and cut costs for further treatment by 95% [95]. The dependence of the phase behaviour of microemulsions on temperature [9, 40] and salt concentration [41] can also be used in order to recover surfactants and other microemulsion components for reuse.

Other approaches for waste reduction and surfactant recovery are based on liquid–liquid extraction. Whereas solutions of anionic surfactants can be readily extracted by oils in extracting columns [39], solutions of non-ionic surfactants must be extracted by hollow fibre membranes [96] or separated from the oil with a centrifuge [97]. A variation of liquid–liquid extraction processes uses supercritical fluids [98]. Volatile contaminants have been separated from the effluent by air-stripping [99] or other evaporation techniques [91]. These processes are, however, often accompanied by excessive foaming. Membrane technologies are therefore preferred. Pervaporation seems to be the most promising method for separating volatile contaminants from surfactant systems [100]. A review of surfactant recovery and reuse is found in Cheng and Sabatini [101].

Improvement of separation processes is certainly one of the future goals in order to reduce the costs of microemulsion technologies for soil remediation. But in the first place, it will be important to convince the authorities of the benefit of these remediation methods in order to obtain permission and funding for further field tests. Experience with real contaminated sites must be extended [102]. In particular, the influence of heterogeneities of soil and contaminant distribution must be further investigated. Modelling can help to understand the relevant processes [103–105]. Further improvements could be made by using geophysical methods for site characterisation and process monitoring [106, 107].

10.3 Microemulsions in enhanced oil recovery

10.3.1 *Why enhanced oil recovery and not alternative fuels?*

Despite growing environmental concerns such as global warming, oil (petroleum) is still the most important non-renewable commodity in today's global economy. It is not only one of principal energy sources, but it is also a raw material for many products like plastics, asphalts and lubricants, to name a few. Nobody living in a modern city can imagine life without petroleum derivatives. Nevertheless, some of the main oil reservoirs are becoming quickly depleted leading to an inexorable slow-down of the oil world production. Besides, it is becoming harder and harder to find new giant oil reservoirs to satisfy the ever escalating demand, not to mention the increasing difficulty surrounding oil politics worldwide and the fact that most of the important alternative energy sources are still in the early stages of industrial or massive implementation. All these leave the world on the verge of a crisis: the world's oil dependence and demand is increasing, while reserves are quickly declining.

At this time and in the near future, there is no available substitute for petroleum-based fuels, if only cost issues are taken into account. For instance, biofuels like ethanol or vegetable oil esters cannot compete on purely economic grounds, without considering other

undesirable issues, particularly because the fertiliser production and crop handling actually consume a high percentage (about 70%) of the energy content of the biofuel. Worst of all, their large-scale development will end up competing for land space with food production.

Another alternative to attain synthetic liquid fuels is the coal-to-liquid route achieved through the Fischer–Tropsch process [108], a proven technology for which raw materials are plentiful and available almost anywhere. Therefore, it is very likely that this technology will be used to provide some of the liquid fuel in the future. Nevertheless, it first has to overcome some of its current drawbacks, e.g. relatively high costs and serious ecological concerns. For this reason, this technology has only been used at an industrial level up to now in countries with restricted economies such as World War II Germany or South Africa under apartheid.

Hydrogen and alcohol fuel cell technologies may help in compensating part of the demand for liquid fuel, but its wide-scale application is still at least two decades away, mainly because of technical and economical issues that need to be surmounted.

On the other hand, both oil-field exploring and well drilling are expensive and laborious tasks. More than 100 years after oil production started, it is very likely that the number of fields yet to be discovered is much less than the number of fields with declining production. Exploration and drilling are becoming less appealing. Based upon this fact, it is crucial and urgent to develop, tune and optimise technologies to enhance the ultimate production yield of the current and abandoned oil reservoirs in order to supply the liquid fuel volume that conventional methods will fail to provide in the near future.

However, it is well known that after an oil well is abandoned, a large proportion of the original oil in place (OOIP) still remains in the ground [109–114]. Generally speaking, primary and secondary oil production technologies are able to recover altogether no more than 30% of OOIP [109, 113]. Initially, an oil well usually produces oil and a small amount of water, and then, particularly while applying water flooding, the most common secondary recovery technique, a mixture of oil and water is produced with a rising water cut as the process proceeds through time [113–115]. Finally, the cost of injection becomes too high to continue the secondary recovery process and the well has to be abandoned with 70% or even more of the OOIP still left in the reservoir.

Therefore, in virtue of all the above, tapping some of the already known 70% OOIP leftover via EOR technologies is probably the best economic solution for overcoming the mega world crises that oil production decline might cause quite soon. Working on exhausted oil wells is appealing not only because about 70% of OOIP is known to be there, but also because a considerable amount of information about them is at hand [112–114], at essentially no cost, when compared to exploring and tapping new fields. Furthermore, drilling and completion costs are to a large extent considerably reduced. Needless to say, EOR is not exempt from economical issues that need to be overcome. Although some of the EOR technologies are already well developed, others still need to be applied at pilot and field scale in order to improve their feasibility and reliability [113, 114, 116].

10.3.2 Why microemulsions?

In this chapter, of all the varieties of technologies known as tertiary oil recovery, only the one known as chemical EOR via microemulsions will be dealt with. Although it is the most complex one, it is the only tertiary technology capable of producing a large

proportion of the oil still remaining in many abandoned wells, at a reasonable cost [109, 113, 114, 117]. Thus, Chemical EOR via microemulsion (a variety of technologies known as micellar flooding, microemulsion flooding, surfactant flooding, surfactant–polymer flooding etc.) may become one of the few real, technological and cost-effective solutions for the predicament of the human race for liquid fuels.

Some of the main characteristics of the EOR via chemical flooding process were discovered during the 1970s and 1980s [109–112, 115, 117–138]. Technical and cost studies in that time also revealed that this technology could potentially increase oil recovery with up to 40–90% of the OOIP [110–114] at an extra current cost of about 10–15 US\$/bbl (i.e. at a maximum 20–30 US\$/bbl cost), and probably even less once the technology is fully developed. Taking into account that an average light crude currently sells at over 60 US\$/bbl (2007) and that the situation seems likely to last for a while due to structural reasons, EOR would leave a profit of at least 30 US\$/bbl. More importantly even, EOR would boost oil world reserves. All these could lead to maintaining the liquid fuel price at a reasonable level, avoiding, thus, a strong impact on world economy, and providing a fair return for producing countries.

After a waterflood, the residual oil remaining in the porous reservoir is trapped by capillary forces. The corresponding interfacial tension between the aqueous and the oil phase is of a few mN m^{-1} [109, 112–115]. Under these conditions, oil production is marginal and the water cut, on the other hand, becomes high [110, 113, 114]. Addition of surface-active substances (i.e. surfactants), however, can lower the interfacial tension by 3–4 orders of magnitude [109, 112–114, 117, 122, 124], which induces the production of more oil and lowers the water cut [113, 139]. Microemulsion flooding tests both at the laboratory and pilot scales have shown that the oil recovery could be more than 60% of the OOIP [110–114], which is about twice the current one. Nevertheless, most of the tests carried out in the field yielded an additional oil recovery of only 10–20% of the OOIP [114, 140], which indicates that the process still has to be improved.

Basically, two types of protocols have been proposed for EOR [110–114, 138]. One of them uses a ‘high’ volume of diluted surfactant solution, while the other uses a ‘small’ volume of highly concentrated surfactant solution. Early results obtained by EOR researchers both in the laboratory and pilot showed that by injecting a properly formulated microemulsion and letting it dilute in the reservoir fluids, a very low tension is maintained even at a surfactant concentration lower than 1 wt.% [113, 114]. This indicates that the low surfactant concentration protocol is technologically feasible to recover a large proportion of extra oil [112–114, 138, 140].

Furthermore, if enough surfactant is used, a zero interfacial tension (i.e. total oil–water miscibility) [112, 117, 141] could be reached with the consequent vanishing of the trapping forces and the recovery of almost all the oil and water present in the swept zone [109–111, 114] through the formation of a single phase (i.e. a bicontinuous microemulsion) containing the trapped oil and surfactant solution. Current formulation know-how indicates that a rather large concentration of surfactant (and co-surfactant), say at about 10%, is required to produce such a microemulsion [137, 141]. Moreover, about 10% of the pore volume of the surfactant solution is needed to sweep the whole reservoir and displace the oil effectively. It is worth mentioning that keeping the crude oil and the surfactant solution as a single phase is not an easy task; actually, such a single phase generally ends separating into three phases [115, 138], one of them a microemulsion, but it does not mean that the

recovery would not be effective. Therefore, although technologically feasible, the complete solubilisation of all the crude oil in a single-phase microemulsion produced by conventional surfactants might not be an economically attractive operation because it requires a large amount of expensive surfactant.

10.3.3 Basic scientific and technical problems

There are three fundamental and one economic issue that need to be addressed before a microemulsion flooding is applied as a routine of oil recovery technique. The first issue is to design a so-called 'optimum' formulation, to attain either total oil miscibility in a single-phase microemulsion (i.e. zero interfacial tension) or an extremely low interfacial tension, typically 10^{-3} mN m⁻¹ or lower, required to mobilise the oil phase through the porous reservoir [109, 112–115]. The second issue is to secure the optimum formulation and to maintain it throughout the whole process while fluids move from the injector to the producer wells. The third fundamental issue is to wrap up a process that involves a sequential injection of a number of fluid volumes, so-called slugs, to displace the oil effectively. The typical slugs, used in chemical EOR, are the preflush, surfactant–co-surfactant, polymer and chase-water slugs. Another slug formed in place is the one known as the oil bank.

The first fundamental issue is easy to reach since it is obtained in the laboratory where all the conditions are reasonably under control, while the second and the third ones are not because they have to be achieved in the field at a much larger scale under a more complex set of conditions and during a much longer time. Before implementing an EOR production routine at industrial scale the three fundamental issues have first to be resolved both at the laboratory and pilot scale; thereafter, a significant economic analysis could be carried out.

10.3.3.1 Attaining optimum formulation

The optimum formulation is a surfactant system with which maximum oil recovery can be achieved. For that purpose, the interfacial tension has to be as low as possible and the oil solubilisation in the microemulsion as large as possible [15, 115, 121, 123, 127, 140, 142–144]. In general, formulation is a concept that tunes the properties of a water–oil–surfactant system such that it can be used for the certain application (see Chapter 3). Extensive studies on the optimum formulation for EOR and various other applications have shown that many variables have to be considered to achieve an ultra-low interfacial tension at relatively low surfactant concentration, or the occurrence of a single-phase bicontinuous microemulsion at high surfactant concentration [15, 143, 144].

It was a century ago that researchers started to study the factors affecting the behaviour of water–oil–surfactant systems but it is only with the introduction of Winsor's R theory (1954) that the formulation effects could be interpreted. Winsor's R theory was the first 'qualitative' description of the formulation, paving the way to an understanding of how intermolecular interactions among the different chemical species present in a system are related to its behaviour. Throughout the following decades, several empirical experimental correlations such as the phase inversion temperature (PIT), semiempirical ones such as the cohesive energy ratio (CER), and models based on thermodynamics such as the surfactant affinity difference (SAD) or the hydrophilic–lipophilic deviation (HLD) [15, 143, 144] led

to a quantitative description of the formulation of water–oil–surfactant systems. Thanks to these studies and numerical data [145], it is possible to roughly determine an optimum formulation with a simple pocket calculator (see Chapter 3 for more details).

In spite of many sources of inaccuracy with real products and phases, research on how to reduce the oil–water interfacial tension or to increase the microemulsion solubilisation capability, which is essentially the same, has exhibited a steady improvement from the 70s until to the beginning of the 90s. At the same time, another main target related to EOR, which was to increase the formulation robustness, was not reached because robustness was found to be inherently inverse to performance; in other words, the larger the solubilisation or the lower the interfacial tension, the narrower the formulation variable range over which it takes place [109]. Some apparent exceptions to this general rule [109–111] are still far from being well understood. During the same period of time, several rules for increasing the surfactant performance were proposed, among them (i) to increase both the numerator and denominator of Winsor's R ratio, (ii) to add lipophilic and hydrophilic linkers and low molecular weight polymer additives and (iii) to use surfactant mixture containing surfactants with intramolecular mixtures [143, 144]. Later new amphiphilic structures (so-called extended surfactants) were designed and synthesised. These new surfactants were found to form a single-phase microemulsion with hydrocarbon oils at a surfactant concentration as low as 2 wt.% [14] and to be particularly suited for improving the performance with polar oils for other applications [146–148].

10.3.3.2 Formulation compatibility with reservoir and fluids

When an optimum formulation is sought to be effective to displace the oil, the complex reservoir conditions cause a lot of complications likely to dramatically affect the expected ultra-low interfacial tension value and the phase behaviour (i.e. the surfactant capability to solubilise oil) [109, 110, 119]. For example, the chemical composition of the different slugs, but specially that of the surfactant one, will change in time and space (with the concomitant change in system phase behaviour) once the aqueous solution containing surfactants, co-surfactants, polymer and electrolytes, is brought into contact with the connate aqueous and oil phases and the surface of the porous reservoir [115]. This situation is even more complex because most of the properties and phenomena involved are also sensitive to changes in temperature and pressure [115, 117, 119, 132, 149], which frequently take place in the reservoir during production. All these require that the formulation of each slug be designed such that the variations they might undergo cancel out or compensate each other so that changes do not significantly affect the surfactant performance in displacing the oil through the porous reservoir. In that way, the whole process, not a particular slug or formulation, would be robust. The following are the main factors found to alter the different slug action and performance.

Pressure

Generally, the reservoir pressure is not high enough to produce a significant change in the surfactant or polymer slug. However, the oil phase is normally much more compressible than the aqueous phase [132, 149]. Additionally, it may contain some dissolved gases [141]. Therefore, oil density and oil chemical composition may be quite different from what is observed in the laboratory. Furthermore, the apparent oil equivalent alkane carbon

number (EACN) may be affected to some extent by these two phenomena [132, 149, 141]. Since optimal formulation is very sensitive to a small change in EACN [120–124], reservoir pressure may indirectly affect the interfacial tension value or the solubilisation greatly. Thus, when designing the surfactant formulation, it is important to take into account that the samples of ‘dead’ oil used in laboratory experiments might have an EACN quite different from those of the ‘live’ oil actually found in the reservoir.

Temperature

Temperature can affect to some extent essentially all the properties of any of the slugs as well as the chemical species they are constituted with. Temperature influences phase behaviour, interfacial tension, electrolyte dissolution, surfactant and alcohol adsorption, and precipitation. It also affects pressure, viscosity, density, and gas concentration in the oil phase, EACN etc. Furthermore, high reservoir temperatures can induce surfactant and polymer chemical degradation. Therefore, temperature is a main factor to take into account when designing the surfactant and the polymer formulas, particularly those that include polyethoxylated non-ionic. Nevertheless, most of the problems caused by the reservoir temperature are relatively easy to solve by formulating the slugs with adequate components [110, 111, 150]. If the reservoir temperature is too high (the chemicals will typically stay in the reservoir for more than 1 year) surfactants and polymers may degrade; therefore, selecting them appropriately is crucial.

Chemical composition

As well as temperature, chemical composition affects all the system’s properties. Thus, one needs to consider any parameter that could alter the composition to such an extent that the formulation is no longer ‘optimal’ and thus might not perform effectively enough.

- *Salinity*: Salinity plays at least two important roles, namely it maintains the integrity of the reservoir and it balances the physicochemical environment so that surfactant formulation stays close to optimal. Thus, ultra-low interfacial tension and oil solubilisation are very sensitive to salinity. Mixing of the surfactant slug with connate water may alter the surfactant formulation mainly due to dilution and to the incorporation of new electrolytes to the formula. Adsorption and desorption of electrolytes, particularly divalent cations, onto or from solid materials such as clay, will also change the salinity of the aqueous phases to some extent and may cause surfactant precipitation, which is however not always an adverse effect [151]. In order to attenuate the undesirable salinity effects on formulation, surfactants able to tolerate salinity changes [109], high salinity [150] and the presence of divalent ions [112] may be used.
- *Surfactant composition*: Surfactants are the critical substances in lowering the interfacial tension. Therefore, all processes likely to change the surfactant composition have to be taken into account. For example, surfactant adsorption and absorption, the dilution of the surfactant containing solution, chemical reactions, degradation and precipitation may occur. All these processes may cause a considerable surfactant concentration drop and thus a chromatographic separation effect, which could result in a surfactant formulation that is no longer ‘optimal’. Dispersion, on the other hand, affects the concentration profile. Such effects could be attenuated or compensated by one or more of the following actions: (1) injecting a sacrificial agent slug (see next section) [113, 114];

(2) injecting the surfactant slug with a salinity gradient [109, 114, 117, 131]; (3) injecting two consecutive polymer slugs with quite different salinity, according to the so-called salinity shock [109]; and (4) adding special polymers and other additives [110, 111, 113, 136]. It is also worth mentioning that surfactant precipitation does not always cause a negative effect; sometimes, it helps in enhancing the displacement of the oil through the porous media by indirectly improving the sweep efficiency of the surfactant slug [151]. An important percentage of the surfactant will be lost in the irreducible residual oil that ends up trapped in the porous medium after applying a microemulsion flooding protocol, particularly in globules caught in unconnected pores [109, 115, 117, 141]. This can be remediated by injecting the right surfactant slug volume at a concentration high enough so that the loss would not significantly affect the surfactant slug performance [117].

- *Polymer composition:* Polymers are essential for controlling the surfactant slug mobility and dispersivity; the efficacy of the polymer depends on the polymer composition. Nevertheless, polymers are very likely to undergo different processes that largely change their concentration and structure. Polymers suffer at least one of the following degradations: mechanical, chemical, thermal and bacterial. They also undergo deposition, excessive adsorption, entrapment, inaccessible pore volume. Besides, they frequently present incompatibility with the surfactants [109, 115, 138]. However, polymers have shown to work relatively well in most chemical flooding conditions [113, 114, 116, 139, 140]. For instance, partially hydrolysed polyacrylamides have been found to work well even in a high temperature reservoir [139].
- *Alcohol composition:* Just as electrolytes do, alcohols help to balance the physicochemical environment in order to keep the surfactant formulation close to optimal, according to the so-called $f(A)$ or $\phi(A)$ effects discussed in Chapter 3. Besides, even so some surfactant formulations do not contain alcohols, they are often added into microemulsion systems as co-solvents (particularly in those containing anionic surfactants) to improve the solubility of the main surfactants and prevent the formation of highly viscous meso-phases [114] such as liquid crystals, which are additionally known to stabilise the emulsions that may be formed. Alcohols can also change the surfactant partition coefficients which has a great effect on the oil recovery efficacy [110, 111].

10.3.3.3 Continuous injection process

Typical EOR surfactant–polymer flooding operations include a sequence of slugs (see Fig. 10.3) that are injected into an oil reservoir [109, 113, 114, 119]. The main idea is to wrap up a process to recover most of the oil still in place (at least much more than what waterflooding does) by preserving at the correct level the main characteristics and functions of the different slugs, particularly the surfactant one, as they pass through the reservoir from the injector to the producer wells. Some of the typical slugs and their main features are described below.

The preflush

The preflush (or preliminary injection) is a slug applied to ‘prepare’ the reservoir to help in protecting the surfactants and polymers against salinity effects and adsorption on the

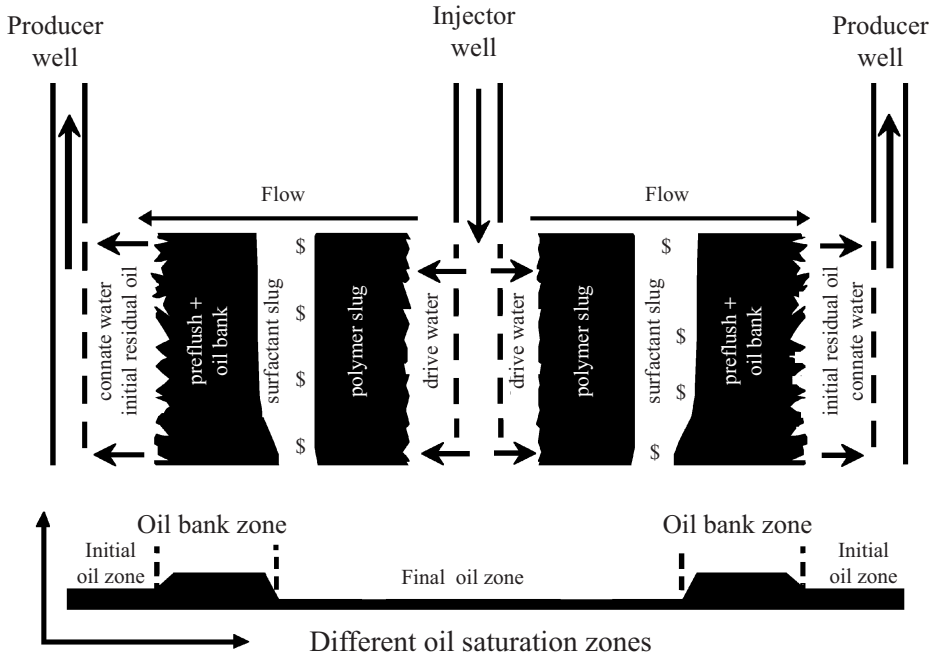


Figure 10.3 Schematic diagram of the oil saturation zones as a function of the different slugs of a typical surfactant–polymer flooding operation.

rock surfaces [114]. In the following some of the commonly designed preflush slugs, which could typically account for 5–10% of the pore volume of the reservoir, are described.

- An alkaline solution is injected as a slug of a surfactant–polymer flooding operation to change the rock surface zeta potential to a negative value. Thus, commonly used anionic surfactants (e.g. petroleum sulphonates) would adsorb less [136]. Alkaline preflush can also alter the rock wettability, although it is not really known whether a water-wet or oil-wet medium is best to prevent surfactant adsorption and chromatographic fractionation. However, alkaline fluids would also induce undesirable effects such as oil emulsification and chemical species precipitation which eventually might cause some plugging. Note that some plugging may improve the sweep efficiency of the surfactant slug, which, in turn, increases oil recovery [151].
- A low salinity water drive could be injected to induce divalent-ion desorption from the porous medium through ion exchange and their subsequent washing away to avoid the main surfactant precipitation as a calcium salt.
- A so-called sacrificial flush is a solution containing cheap surfactant substitutes (e.g. lignosulphonates) likely to adsorb on the rock surface. Such a slug could be injected to prevent or reduce the adsorption from the surfactant slug, thus reducing losses (and cost) and formulation alterations. It also prepares the reservoir fluids to reach the optimal formulation in an easier and faster way.

The surfactant/co-surfactant slug

After the oil bank this is the most important slug because surfactants are the most expensive ingredients, as well as the critical ones from the oil displacement point of view. Once the surfactant slug contacts the oil globules these get mobilised and start moving through narrow necks of the porous reservoir. Afterwards the oil globules coalesce (because optimum formulation is associated with low emulsion stability) to form the oil bank. The oil bank thus formed is then pushed, displaced and propagated by the surfactant slug through the reservoir from the injector to the producer well (see Fig. 10.3). To assure a high oil recovery efficacy and a low water cut, the surfactant slug must stay stable both at the rear and front edges, its formulation should remain optimal or close to it and its sweep efficiency should be high, as close as possible to 100% of the porous volume. For instance, it has been shown that the performance of the surfactant slug is higher when the salinity varies as a decreasing electrolyte concentration, according to the so-called salinity gradient, which is a clever way to increase the displacement efficacy both at the front and rear edges [109, 114, 117, 131, 152]. At the front (leading) edge of the surfactant slug the transition between Winsor II and Winsor III takes place leading to a low interfacial tension between oil and the microemulsion, which improves the displacement of the surfactant slug and oil bank. Because of the ultra-low interfacial tension it also induces the early formation of the oil bank. At the rear edge of the surfactant slug, on the other hand, the transition between Winsor I and Winsor III takes place leading to a low interfacial tension between the aqueous polymer solution and the microemulsion (see supersolubilisation in Section 10.2.3.4), which improves the displacement of both the surfactant and polymer slugs. These features prevent microemulsion trapping, oil redispersion and emulsion formation by attenuating dispersivity and capillary forces [109, 114].

Similarly, alcohols can also induce a dramatic boost in oil recovery. The following two examples illustrate the important role alcohols can play in EOR: (1) Pithapurwala *et al.* [110, 111] found that by changing the alcohol (i.e. the alcohol structure) a dramatically change in oil recovery could be attained (e.g. 11, 14, 27, 92% of the OOIP). (2) Additionally, Shah [109] found that alcohol plays an important role on the oil flattening time, which is the time that an oil drop takes, under a specific environment, to become flat. He found that systems with lower flattening time showed the higher oil recovery efficiency. The volume of the surfactant slug typically ranges from 5 to 50% of the porous volume; it contains surfactant (0.1–10 wt.%), co-surfactant (0–5 wt.%), brine (0–reservoir salinity) and often polymer (0.05–0.2 wt.%) [113, 114, 116].

The pusher slug

The polymer slug that comes after the oil bank and surfactant slugs is the third one of importance. Among other functions, it controls the mobility of the surfactant slug enhancing its efficiency to sweep a large proportion of the whole porous medium and thus increasing the oil recovery. In order to prevent both the redispersion of the mobilised oil and dispersion of the surfactants, both the displacement of the oil bank by the surfactant slug and the surfactant slug by the polymer slug must be stable (i.e. without fingering nor stable emulsion); consequently, each slug must be displaced by a more viscous fluid [114, 115]. The polymer slug is often designed to exhibit a high viscosity at the front contact with the surfactant slug so that an almost piston displacement is warranted. It has

been shown [109] that when the injected polymer slug is actually made of two polymer slugs with quite different salinities (in a process called salinity shock), the oil recovery is appreciably increased, while the surfactant loss is greatly reduced. Generally, the volume of the polymer slug ranges from 15 to 100% of the pore volume; it contains polymer (0.05–0.2 wt.%) and brine (0–reservoir salinity) [109, 114, 139, 140]. Additionally, a polymer slug helps in lowering the chemical costs by decreasing the volume of the surfactant slug to be injected.

Driver or chase water slug

The driver or chase water slug is a solution injected after the polymer slug whose viscosity progressively decreases, ending up as brine [109, 115, 119, 133, 141]. This slug is used, instead of a large polymer slug, to cut down the operation and the chemical costs.

Oil bank

Finally, the oil bank is not an injected slug but it is formed when the oil globules displaced by the surfactant slug coalesce, thus forming a two-phase flow pattern. Thereafter, it grows and propagates as it contacts at its leading edge more disconnected oil globules as the surfactant slug displaces it towards the producer wells [142]. The oil bank early formation and its stable propagation through the reservoir are of paramount importance to warranty the recovery of a high percentage of the OOIP [109].

The thickness of each slug decreases as they move radially from the (central) injector to the (peripheral) producer wells, due to both the geometry of the flow and the fact that the components of the slug are retained or incorporated into the oil phase. For example, for a well pattern in which the separation distance between injecting and producing wells is 100 m, a rough calculation, without considering surfactant loss, yields, for a surfactant slug volume of 10% of the pore volume, 31.6 m for the initial thickness and about 5.1 m for the final one. After considering surfactant loss, the surfactant slug would reach the producer wells much slimmer. This could help in designing a criterion to know if the different slug volumes injected into the reservoir are larger than what is really necessary. As a rule of thumb, it may be said that the volume of any of the injected slugs should be large enough to sweep the whole reservoir pore volume without losing its integrity.

10.3.4 Current state-of-the-art in enhanced oil recovery

Laboratory-scale studies, computer simulations and field trials have been performed with the same common goals mentioned above: (1) to enhance the performance of the surfactant formulation in attaining ultra-low interfacial tension and high solubilisation capability; (2) to maintain the optimal formulation during the process; (3) to improve the surfactant–slug sweep efficiency in the porous medium. The underlying idea is that a high oil recovery efficacy should be reached by achieving each of these goals.

10.3.4.1 Laboratory research

A lot of studies on formulating microemulsions for EOR were carried out in the decade 1973–1983 [109–112, 115, 117–131] where crude oil prices were high. About three billion

dollars were spent on R&D to attain what is essentially the current know-how. Thereafter, it was essentially only in China that government-supported R&D groups have maintained a high research activity in EOR [113]. In the rest of the world and due to unfavourable economics, only a few laboratories financially supported by national oil companies dedicated some R&D funding to EOR [110, 112–114]. Researches studying microemulsions focused on improving the fundamental understanding [15, 143, 144] and finding many other new applications [15, 27, 143, 144, 153], e.g. soil remediation, cleaning, detergency (also best performed at optimum formulation), water solubilisation of oil (soak-only detergency, oil extraction) and even drug delivery systems. Additional different formulations were developed to lower surfactant loss and mixture chromatographic separation [136].

These research activities, though targeted at other applications, have helped both in widening and deepening the knowledge on surfactant system, which have increased the value of microemulsion know-how, thus making it readily available for the future of EOR, when the oil prices would rise again, as it is currently the case. Some examples of these developments are the anionic–cationic surfactant mixtures that have shown a synergistic effect in lowering interfacial tension and increasing oil solubilisation [143, 144]. Their use in EOR would probably have a positive impact on the percentage of oil recovered. Similarly, some formulations containing anionic surfactants and long-chain alcohols exhibited an increase in solubilisation power with bicontinuous microemulsion at a surfactant concentration as low as 2 wt.% [15, 143, 144]. Further developments from such works are the so-called extended surfactants which are able to lower oil–water interfacial tension at very low surfactant concentration, to form bicontinuous microemulsion with hydrocarbons at a surfactant concentration about 2 wt.% [14], and to exhibit a high solubilisation of polar oils for pharmaceutical and cosmetic applications [146–148]. All these studies led to a better understanding and allowed us to develop very simple models for describing the formulation of surfactant systems [15, 112, 113, 143, 144]. Most of the studies in microemulsion flooding have focused almost exclusively on the performance of the surfactant formulation and on finding cheaper ways of implementing the process. Research in polymer performance, on the other hand, has evolved from other areas and applications different from microemulsion flooding. Since the end of the 70s, both polymer science and technology have undergone a dramatic expansion which can help in improving all the polymer functions and attenuating all the polymer drawbacks. Although polyacrylamide is still the main candidate for chemical EOR [113, 117, 139, 140], new polymers with fancy rheological behaviour could greatly improve the sweep efficiency of the surfactant slug by attenuating phenomena such as fingering and hydrodynamic dispersivity. They can also lower the incompatibility with the different chemical species present in the reservoir and in the different slugs (especially with the surfactant slug) and surfactant loss. Similarly, they can be more tolerant to divalent ions, high salinity and temperature. Such polymers may nowadays look prohibitive from an economic point of view for an application-like EOR in which a large amount of polymer is entirely lost after being injected into a well to perform some particular functions. Nevertheless, in order to improve the current stage of the surfactant performance in recovering higher percentage of the OOIP, it is a must to try to incorporate new polymers in the chemical EOR research, regardless their costs, aiming just to enhance each of their functions and finding the limits.

10.3.4.2 Computer simulations

Computational simulations are always welcome since they can be used to explore features that are impossible or difficult to test or monitor experimentally. Simulations could help to design slug formulas and size, which can greatly impact the economy of the operation [134, 154] so that each slug performs its role throughout the whole reservoir. However, real microemulsion flooding involves a great number of system properties which are interconnected and influenced by the chemical composition, the temperature, the pressure and the porous reservoir [109, 115, 119, 131, 132, 135, 149]. In addition, some of the phenomena, like the fluid flow, are sensitive to gravity [119]. To date the only properties relatively easy to predict and to monitor are the changes induced by temperature and pressure. Since these two parameters are likely to affect the performances of the different slugs, computer simulation of their effect on the surfactant and polymer slug properties as well as on processes in the reservoir are of great help. Unfortunately, due to the complexity of the interconnected processes, interfacial tensions or the phase behaviour are almost impossible to simulate under real reservoir conditions. On the other hand, in spite of intents to provide computational and modelling tools to simulate the phase behaviour or the compositional mass balance of surfactant (UTCHEM) [154], it may be said that computational simulation is still lagging too far behind to be of practical use in an EOR real case scenario.

10.3.4.3 Field research

Several pilot field tests carried out at the end of the 70s, essentially showed three things that were also observed at the laboratory scale. (1) First, EOR by surfactant flooding is a feasible process [109, 113, 114, 117, 138, 140], particularly for low viscosity crudes, low salinity and low temperature reservoirs [116]. (2) Second, a lot of precautions have to be taken into account because of the difficulties that arise from unpredicted formulation changes due to surfactant adsorption, electrolyte desorption, reservoir heterogeneity, insufficient information on the porous medium morphology and fluid pattern [113, 114, 119, 138]. (3) Third, many formulations containing cheap surfactants such as petroleum sulphonates work well [113, 114, 128, 150] though they could probably be improved.

Similarly, many researchers have studied alkali, alkali-polymer and alkali-surfactant-polymer (namely ASP) recovery processes [110, 140, 155]. All these chemical EOR methods are based on the fact that injection of aqueous alkaline solution induces the in situ formation of oil natural surfactants through acid-base chemical reaction [116] in addition to the reservoir rock conditioning effect. In spite of the great effort and the encouraging laboratory results, pilot test outcomes for the first two have been poor [113, 117]. On the other hand, in spite of the relative low chemical cost compared to surfactant-polymer floods [113, 116, 155], hopeful laboratory tests [113, 114, 155, 156] (some of which claim an oil recovery greater than 80% of the OOIP [113, 114]), and some excellent pilot test results [113, 140], the ASP method has not found widespread applications [113, 116]. This suggests that ASP is not a mature technology, probably because the involved phenomena (e.g. change of wettability, spontaneous emulsification, emulsion flow through a porous medium, sensitivity to pH changes) are more complex than what had been first recognised [116, 155].

10.3.5 Future 'GUESSTIMATES'

Even though there is a great potential in the chemical EOR methods to considerably expand the World oil reserves, they still remain marginal [116, 117] more than 30 years after an unprecedented research effort to understand how petroleum is trapped in an oil reservoir and to develop technologies was carried out. The drop of crude oil price in the early 80s has probably been the main reason for this but a second main limiting issue still to be settled is the incomplete understanding of the interconnection between all occurring processes.

Chemical EOR is surely one of the petroleum industry's most complex, costly and risky operations, though so attractive that it is one of the current challenges of the oil industry. Its implementation in an actual field routine demands a great deal of creative thoughts and a great amount of chemicals and energy. Taking this into account, it is believed that EOR technology via microemulsion flooding faces two uncertainties which will determine its future.

1. How could scientific and technological challenges be overcome? The main problems to be dealt with are to maintain the optimum formulation of the surfactant slug during the process and to improve the sweep efficiency of the main surfactant slug.
2. How could operation and chemical costs be lowered? One important cost factor is the surfactant itself and new surfactant formulations are needed, which are capable of solubilising a wide variety of crude oils at low surfactant concentrations, i.e. 2 wt.% or even lower. Another factor that could reduce costs considerably is implementing an EOR operation in the right moment, i.e. primary instead of secondary or tertiary. Generally speaking, from the early studies undergone in the 70s, EOR via microemulsion flooding technology has been designed to be applied after the secondary recovery [112, 115, 119], i.e. as tertiary recovery. It is important mentioning that during a secondary recovery, e.g. by waterflooding, the oil saturation in the porous medium decreases down to a value around 0.3 [112, 113, 115]. Thereafter the oil remains mainly as disconnected globules [109, 113, 115, 129] trapped by capillary forces [109, 115, 117]. Is it necessary to wait till such a condition is reached to apply a chemical EOR technique? How about implementing, for new oil wells, a microemulsion flooding routine just after primary recovery? Unpublished trials [157] suggest that starting a microemulsion flooding routine just after primary recovery could result in an increase in oil recovery efficacy of more than 30% when compared to recovery attained by the traditional microemulsion tertiary flooding protocol. The high increase in oil recovery observed when an oil bank is previously injected [109] supports this inference. Therefore, for new oil wells a microemulsion flooding routine would have to be tried as a 'secondary' recovery routine or enhanced waterflooding. In addition, an implementation after primary recovery could help in increasing the oil ultimate recovery and preserving the reservoir from damages due to the wrong use of different chemical slugs.

Many of the EOR protocol sequences that have been used to date for low surfactant concentrations use a surfactant slug formulated with some polymer to improve its sweep efficiency [109, 138]. Taking this into account and considering the new polymer and surfactant developments, a future surfactant slug would have to be formulated with the new polymers and surfactants. Such a slug would provide the sites (some polymer segments)

to the surfactant to stay adsorbed and to promote micelle formation, which would reduce surfactant loss [109, 136] and increase the salinity tolerance [109]. Besides, in presence of high solubilisation surfactants, such a slug would be able to dissolve the oil in a single-phase microemulsion at a surfactant concentration at most of 2 wt.%. Furthermore, the relatively high viscosity of the slug would probably enhance the cleaning power of the slug.

Because of the diversity, interconnection and extreme complexity of the involved phenomena that take place during an EOR operation, only a few people with the down-the-bench expertise are currently available worldwide, and most of them are close to retirement, hence, great deal of their know-how is likely to be lost soon. It is thus a matter of extreme urgency to train a new generation of scientists and engineers with the proper understanding of both the physical chemistry and actual field issues, to tackle the present and future challenges of chemical EOR. This matter will probably require a concerted commitment between academic and industrial partners.

10.4 Degreasing of leather

10.4.1 Washing processes

When dealing with washing processes such as degreasing two questions have to be asked. First, how much amphiphile, i.e. surfactant, do I need to solubilise the natural fat and under which conditions does the system wash, i.e. degrease most effectively. The first question is a matter of efficiency. To determine the efficiency of a microemulsion system the pivot point for microemulsion phase behaviour, the so-called X-point, has to be determined. Depending on the temperature T and the surfactant mass fraction γ the phase boundaries of a ternary microemulsion system resemble the shape of a fish [158, 159]. The point where fish body (three-phase region) and fish tail (single-phase region) meet is the X-point or fish-tail point, which marks the onset of the single-phase microemulsion region and is defined by the least surfactant mass fraction needed to totally solubilise water and oil (see Chapter 1 for more details). The second question was already addressed by Benson *et al.* [160] together with Kahlweit and Strey [161], who found that the oil removal in a washing process reaches its maximum in the three-phase region of the respective microemulsion system (see Chapter 8, Fig. 8.12). The three-phase region of a microemulsion system is closely connected to the interfacial tension between water and oil σ_{ab} , which becomes minimal at the mean temperature of the three-phase region. For efficient microemulsion systems σ_{ab} drops to ultra-low values of 10^{-3} – 10^{-4} mN m⁻¹. Thus, for the efficient degreasing of animal skins one has to know the location of the three-phase region and hence of the X-point.

10.4.2 Leather degreasing via microemulsions

The large-scale application of microemulsions in leather degreasing was motivated by questioning current industrial processes for degreasing due to potentially environmental concerns. Of relevance for leather degreasing were mainly two processes, a solvent-based one and a water-based one. The surfactants showing the best performance in the latter

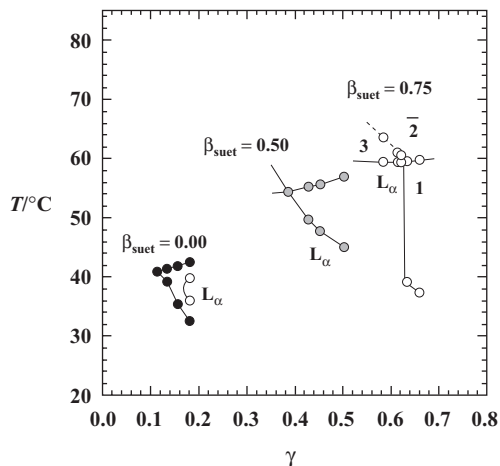


Figure 10.4 Phase diagrams of the systems $\text{H}_2\text{O}/\text{NaCl}$ -rape oleic acid methyl ester/suet-Lutensol[®] AP9 at $\phi = 0.50$ and $\epsilon = 0.10$. The parameter β corresponds to the mass fraction of suet in the mixture of suet and rape oleic acid methyl ester. With increasing β , the phase behaviour is shifted to higher temperatures and surfactant mass fractions. Because of the dominance of the L_α -phase a phase diagram at $\beta = 1.00$ could not be obtained.

process are alkyl phenol ethoxylates. As these surfactants decompose during effluent treatment and form chemicals, which have an endocrine-disrupting effect on life-forms, alternatives had to be found, which show a comparable or even better degreasing performance. In the following we present a way how to eco-friendly degrease animal skins via microemulsions and clarify the so far unidentified mechanism of degreasing.

10.4.2.1 Phase behaviour of suet microemulsions

Benchmark

Standard surfactants for water-based degreasing of animal skins are non-ionic alkyl phenol ethoxylates. The phase behaviour of the benchmark Lutensol[®] AP9 was characterised in the system $\text{H}_2\text{O}/\text{NaCl}$ -rape oleic acid methyl ester/suet-Lutensol[®] AP9. As natural fat, suet consists mainly of triacylglycerols, which can only be solubilised at high surfactant mass fractions [162]. To enhance the efficiency of the system, rape oleic acid methyl ester was used as co-oil. The mass fraction of suet in the mixture of rape oleic acid methyl ester and suet is given by the parameter β . The salt mass fraction in the water phase ϵ was kept constant at $\epsilon = 0.10$ and the phase behaviour was determined at equal volume fractions of water and oil, $\phi = 0.50$. The T - γ cuts presented in Fig. 10.4 show that rape oleic acid methyl ester is efficiently solubilised by Lutensol[®] AP9. The X-point is located at $\tilde{T} = 40.65^\circ\text{C}$ and $\tilde{\gamma} = 0.119$ and a liquid crystalline lamellar phase (L_α) extends in the single-phase region. The 'fish' is distorted towards lower γ , which is typical for technical surfactants. Upon increasing the mass fraction of suet to $\beta = 0.50$ the phase behaviour shifts to higher temperatures and surfactant mass fractions. The L_α -phase now extends below the lower phase boundary. This trend continues to $\beta = 0.75$. The X-point is located

at $\tilde{T} = 59.40^\circ\text{C}$ and $\tilde{\gamma} = 0.628$. The L_α -phase dominates the phase behaviour. As a result the lower phase boundary becomes steep and the X-point is difficult to detect. Because of the dominance of the L_α -phase a system with $\beta = 1.00$ could not be obtained. Thus, the solubilisation of suet by Lutensol[®]AP9 is rather limited.

Eco-friendly Surfactants

In contrast to alkyl phenol ethoxylates the class of fatty alcohol ethoxylates is biodegradable and eco-friendly. Efficient technical surfactants found in this class are Lutensol[®]XL 700, Lutensol[®]TO8, Lutensol[®]AO7, Lutensol[®]AO8 and Eusapon[®]OD. The phase behaviour was characterised in systems of type $\text{H}_2\text{O}/\text{NaCl}$ -suet-technical non-ionic surfactant. The salt mass fraction was kept constant at $\varepsilon = 0.10$ and the oil volume fraction at $\phi = 0.50$. In view of the degreasing process, which is conducted at 30°C , the X-point of the optimal system should be located around 30°C and the formation of the highly viscous L_α -phase should be suppressed. Figure 10.5 presents the T - γ cuts for the respective systems.

In the following the T - γ cuts will be discussed in the order of their efficiency. Because of its comparatively short C-chain length ($i = 10$) Lutensol[®]XL 700 is the most inefficient one of the surfactants. The X-point is located at $\tilde{T} = 50.67^\circ\text{C}$ and $\tilde{\gamma} = 0.678$. A liquid crystalline lamellar phase extends below the lower phase boundary. With increasing C-chain length of the surfactant, i.e. substituting Lutensol[®]XL 700 by Lutensol[®]TO8 ($i = 13$), the phase behaviour shifts to lower surfactant mass fractions as expected [163]. Because of the increased number of ethoxylate groups the phase behaviour also shifts to higher temperatures. The L_α -phase again extends below the lower phase boundary. The efficiency can be further increased by substituting Lutensol[®]TO8 by its longer-chained homologous Lutensol[®]AO7 and Lutensol[®]AO8, respectively. The X-points of the systems are located at $\tilde{T} = 57.09^\circ\text{C}$ and $\tilde{\gamma} = 0.379$ (AO7) and $\tilde{T} = 61.95^\circ\text{C}$ and $\tilde{\gamma} = 0.404$ (AO8).

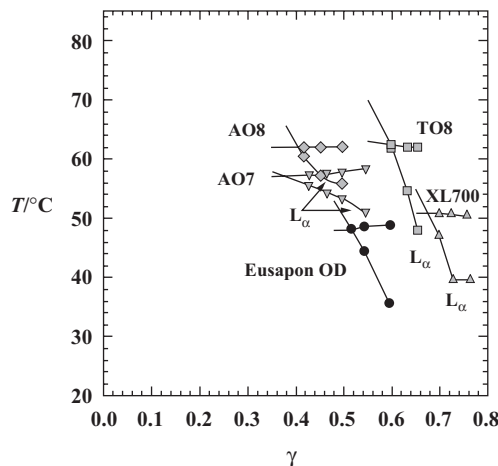


Figure 10.5 Phase diagrams of the systems $\text{H}_2\text{O}/\text{NaCl}$ -suet-technical non-ionic surfactant at $\phi = 0.50$ and $\varepsilon = 0.10$. Although less efficient than Lutensol[®]AO7 and Lutensol[®]AO8, Eusapon[®]OD is the most suitable alternative for Lutensol[®]AP9 as the X-point is located near the degreasing temperature and no L_α -phase forms.

However, the L_{α} -phase in both systems extends over a wide γ -range below the lower phase boundary. The most suitable of the characterised surfactants regarding the degreasing process is Eusapon[®]OD. Although less efficient than Lutensol[®]AO7 and Lutensol[®]AO8 no L_{α} -phase can be observed and the X-point is located near the degreasing temperature, $\tilde{T} = 48.13^{\circ}\text{C}$.

10.4.2.2 Eco-friendly degreasing

The degreasing experiments were performed in the beam house of BASF AG according to recipes for very greasy sheep skins. In seven drums, two skins were degreased at a time. In order to protect the collagen network of the skin the degreasing temperature was kept constant at $T = 30^{\circ}\text{C}$. Prior to the degreasing experiments the New Zealand sheep skins were depickled by adding a short float (30 wt.% of water) containing high amounts of sodium chloride (8 wt.%). For the first degreasing step, surfactant was added (1 wt.%) and the drums were run for approximately 1 h. The short float was then diluted with pure water (70 wt.%). In the following this float will be denoted as diluted float. After drainage of the diluted float the skins were again washed with surfactant (2 wt.%) and water (200 wt.%). In the following this float will be denoted as long float. Finally, the degreased skins were examined by the tanner to evaluate the degreasing performance.

Sheep skins were degreased using Eusapon[®]OD following the above presented procedure in the beam house. Samples were taken from every float and the phase behaviour was directly characterised by visual inspection. The results are presented in the following beginning with the short float.

Short float

Because of the small amount of water in the short float, samples had to be taken by wringing out the sheep skins. A three-phase state at $T = 37^{\circ}\text{C}$ could be observed, where a microemulsion phase coexisted with a fat-excess phase and a water-excess phase as presented in Fig. 10.6. At this point, the occurrence of the three-phase state in the short float was a first evidence for the good performance of Eusapon[®]OD. The three-phase state is closely connected to the interfacial tension between water and oil, in this case water and grease (σ_{ab}) which becomes ultra-low for efficient microemulsion systems. At this point the low interfacial tension ensures a good degreasing performance of the system. More

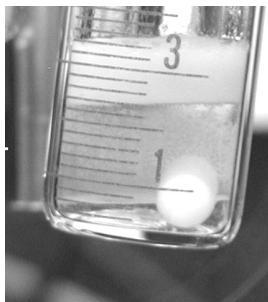


Figure 10.6 Picture of the three-phase state found in the short float at $T = 37^{\circ}\text{C}$. A microemulsion phase coexists with a fat- and a water-excess phase.

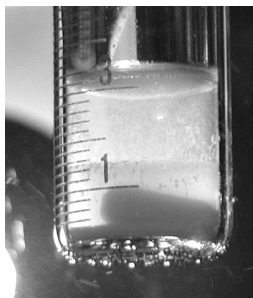


Figure 10.7 Picture of the three-phase state found in the diluted and in the long float at $T = 60^\circ\text{C}$. A microemulsion phase coexists with a fat- and a water-excess phase.

importantly, it could be verified for the first time that microemulsions play an important role in the degreasing process.

Diluted float/long float

Samples were also taken from the diluted and the long float. The characterisation of the phase behaviour resulted for both floats in a three-phase state, which, in contrast to the short float, is not located at $T = 37^\circ\text{C}$, but at $T = 60^\circ\text{C}$ as shown in Fig. 10.7. At the degreasing temperature $T = 30^\circ\text{C}$ now a fat-in-water microemulsion coexists with a fat-excess phase, which is turned into a stable fat-in-water emulsion via shearing.

10.4.2.3 Correlation of phase behaviour and eco-friendly degreasing

The results obtained from the characterisation of the phase behaviour and in the beam house imply that Eusapon[®]OD is a suitable alternative allowing for an eco-friendly degreasing of animal skins. However, the understanding of the so far unidentified degreasing mechanism is the key goal for a continuous development of the degreasing process itself. In order to clarify the role of microemulsions in degreasing additional phase behaviour and interfacial tension measurements were conducted.

T - γ cut and T - γ_b cut

Analogue to other natural fat suet shows charge-dependent fluctuations in its composition. Triolein is the main component of nearly all natural fats and was therefore used as a 'model-fat' for further investigations. Figure 10.8 shows the phase diagram of the system $\text{H}_2\text{O}/\text{NaCl}$ -triolein-Eusapon[®]OD at $\varepsilon = 0.10$ and $\phi = 0.50$. As degreasing takes place at very low values of γ the three-phase region of the system was characterised, as well.

The phase diagram shows that the lower phase boundary of the three-phase region is located above 44°C . This result is contrary to the findings in the degreasing experiments, i.e. the short float, where a three-phase state at 37°C could be observed. In order to understand this discrepancy schematic Gibbs triangles for the characterisation of the phase behaviour and the degreasing experiments are shown in Fig. 10.9. Figure 10.9(a) represents the T - γ cut performed to characterise the phase behaviour of the benchmark Lutensol[®]AP9 as well as the eco-friendly fatty alcohol ethoxylates at equal volume fractions of water and oil $\phi = 0.50$ (see also Figs. 10.4 and 10.5). However, during the degreasing experiments the

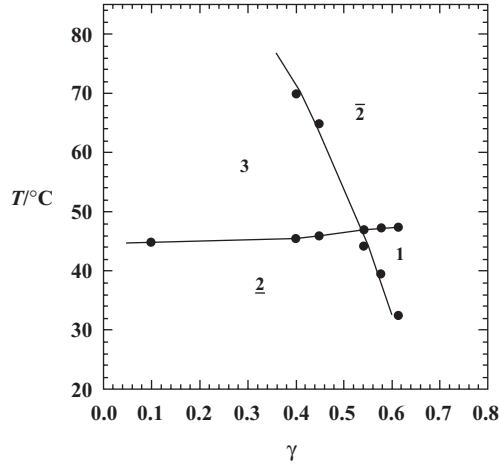


Figure 10.8 Phase diagram of the system $\text{H}_2\text{O}/\text{NaCl}$ -triolein-Eusapon[®]OD at $\epsilon = 0.10$ and $\phi = 0.50$. Single-phase region and parts of the three-phase region are shown.

volume fractions of water and oil in the float vary. Starting with small amounts of water in the short float the amount of water is largely increased in the diluted and in the long float. Thus, the cut performed in the degreasing experiments is a so-called T - γ_b cut, where γ_b represents the mass fraction of surfactant in the mixture of oil and surfactant, i.e.

$$\gamma_b = \frac{m_{\text{surfactant}}}{m_{\text{surfactant}} + m_{\text{fat}}} \quad (10.1)$$

This ‘dilution’ cut is shown schematically in Fig. 10.9(b). To mimic the conditions in the beam house a T - γ_b cut was conducted for the system $\text{H}_2\text{O}/\text{NaCl}$ -triolein-Eusapon[®]OD at $\gamma_b = 0.375$ and $\epsilon = 0.10$. The value of γ_b was derived from the fat content of the float after degreasing. The phase diagrams at constant ϕ (black symbols) and at constant γ_b

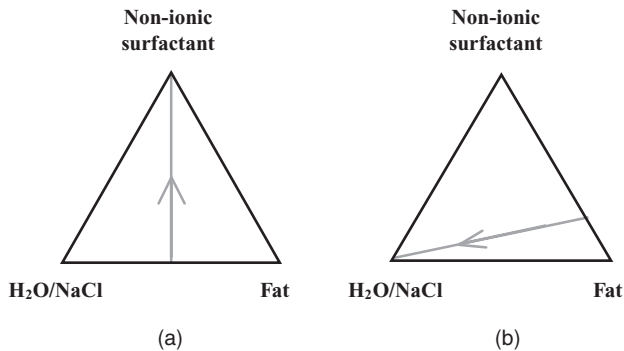


Figure 10.9 Schematic Gibbs triangles for the system $\text{H}_2\text{O}/\text{NaCl}$ -natural fat-non-ionic surfactant. (a) T - γ cut at $\phi = 0.50$; (b) T - γ_b cut with varying water to oil plus water volume fraction.

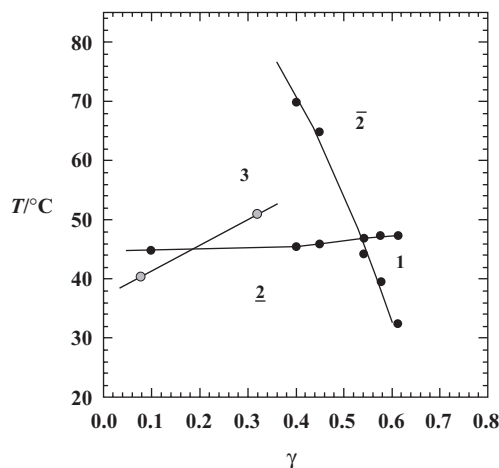


Figure 10.10 Phase diagram of the system $\text{H}_2\text{O}/\text{NaCl}$ -triolein-Eusapon[®]OD at $\epsilon = 0.10$ and $\phi = 0.50$ (black symbols) and lower phase boundary of the system $\text{H}_2\text{O}/\text{NaCl}$ -triolein-Eusapon[®]OD at $\gamma_b = 0.375$ (gray symbols).

(gray symbols) are shown in Fig. 10.10. For the clarification of the degreasing process only the lower phase boundary is important as it is located near the degreasing temperature $T = 30^\circ\text{C}$. For this reason the upper phase boundary was not determined. Because of high emulsion stability only two data points could be obtained at constant γ_b . Compared to the T - γ cut the lower phase boundary in the T - γ_b cut shifts to lower temperatures upon dilution with sodium chloride solution, which is caused by the increasing extraction of the hydrophilic fractions of the technical surfactant from the interfacial film into the water phase. As a result the surfactant remaining in the interfacial film becomes more hydrophobic. Because of the temperature shift the location of the lower phase boundary at low γ in the T - γ_b cut now corresponds to the temperature of the three-phase state observed in the short float.

Ultra-low interfacial tension

The reason for the optimal degreasing performance of the microemulsion in the three-phase region is the ultra-low interfacial tension between water and oil σ_{ab} . Figure 10.11 shows the variation of σ_{ab} as a function of T for the system $\text{H}_2\text{O}/\text{NaCl}$ -triolein-Eusapon[®]OD. In order to mimic the composition of the float a fat to water plus fat mass fraction $\alpha = 0.15$ was chosen, which is the least fat mass fraction required for spinning drop measurements.

The variation of the interfacial tension as a function of T for the Eusapon[®]OD system shows the typical V-shape. The full curve corresponds to a theoretical description in terms of bending energy [164, 165]. The minimum of the interfacial tension correlates well with the mean temperature of the system and is located at $\sigma_{ab} = 0.13 \text{ mN m}^{-1}$ at $T_m = 51.5^\circ\text{C}$. For the benchmark Lutensol[®]AP9 the interfacial tension between water and oil near the degreasing temperature corresponds to $\sigma_{ab} = 0.43 \text{ mN m}^{-1}$. Although the interfacial tension between water and triolein is high compared to efficient microemulsion systems, it is still two orders of magnitude lower than the pure water oil interfacial tension (50 mN m^{-1}).

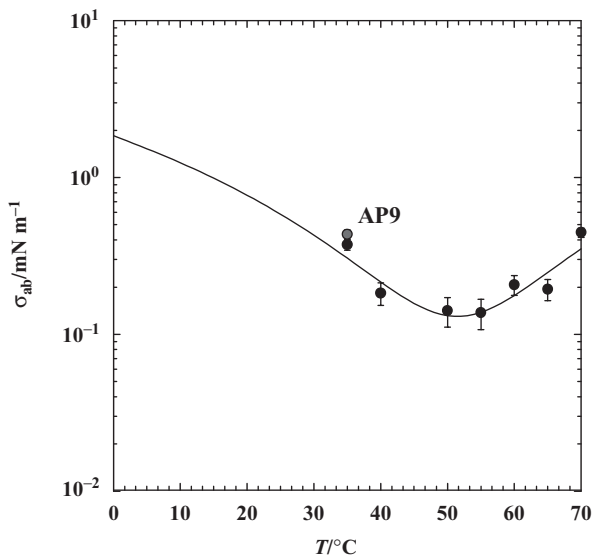


Figure 10.11 Variation of σ_{ab} with temperature for the system $\text{H}_2\text{O}/\text{NaCl}$ -triolein-Eusapon[®]OD at $\alpha = 0.15$ and $\epsilon = 0.10$. The value for the Lutensol[®]AP9 system at $T = 35^\circ\text{C}$ is shown as well.

10.4.2.4 The 'Salt-Jump'

Animal skins were degreased in a three-step process according to the procedure described in the section beam house. In a first step, surfactant was added to depickled sheep skins and the drum was run for approximately 1 h. Note, that depickling means the addition of a short float (little water) containing high amounts of sodium chloride. The mass fraction of salt in the water phase of the short float was estimated to be $\epsilon = 0.21$. After 1 h the short float was diluted with pure water. As a result the sodium chloride mass fraction in the water phase ϵ was instantaneously reduced to $\epsilon = 0.07$. During this process the surfactant to fat plus surfactant ratio γ_b was always constant at approximately $\gamma_b = 0.375$.

The dramatic reduction of the salt mass fraction strongly influences the phase behaviour of the float. The resulting variation of the phase behaviour is the key for the optimal degreasing performance and can be understood as follows. In Fig. 10.12, the variation of the phase behaviour in the course of the degreasing process is shown schematically. The presentation in form of T - γ cuts is for clarity reasons. The fat to water plus fat volume fractions ϕ vary during degreasing, thus the presentation in form of Gibbs triangles corresponds to the real experimental conditions.

In Fig. 10.12(a), the phase behaviour in the short float is shown. The three-phase state of the respective systems is located near the degreasing temperature $T = 30^\circ\text{C}$. Efficient degreasing is a result of the ultra-low interfacial tension between water and fat. Upon diluting the short float with pure water the salt mass fraction in the water phase is effectively reduced from $\epsilon = 0.21$ to $\epsilon = 0.07$. Sodium chloride belongs to the group of lyotropic salts. When the salt mass fraction is reduced the hydration of the surfactant head

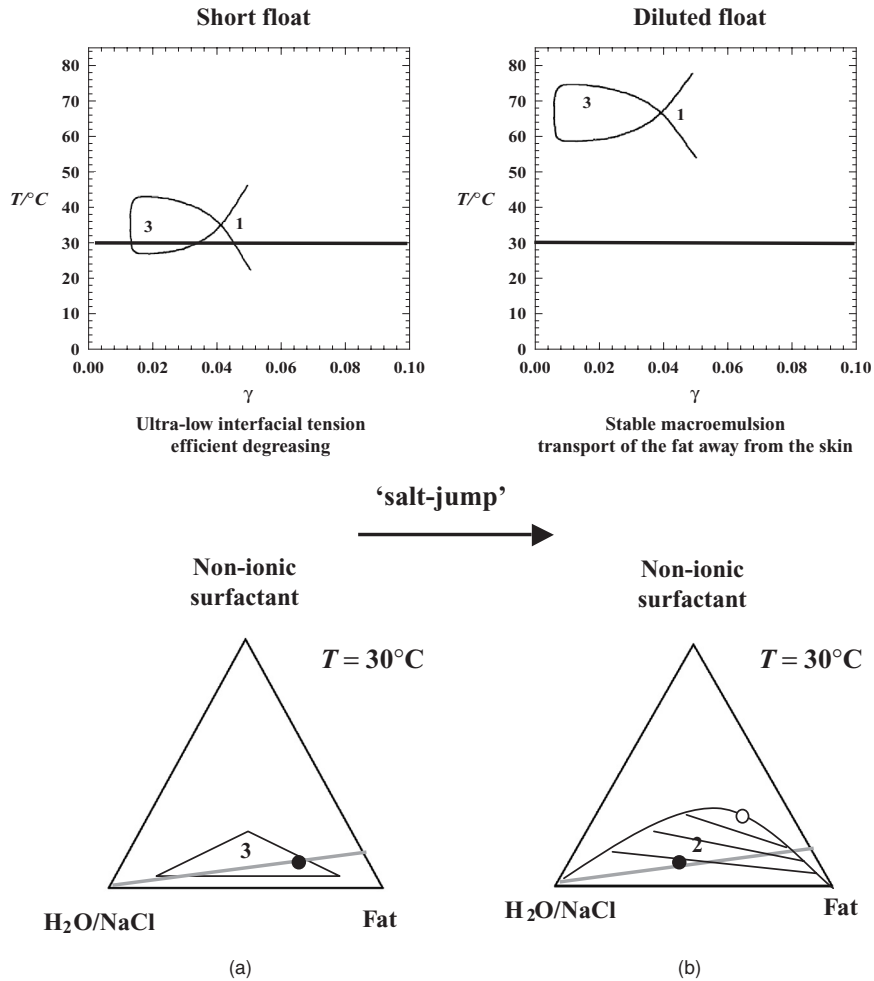


Figure 10.12 Schematic of the variation of the phase behaviour during the degreasing process. In the short float the ultra-low interfacial tension between water and oil ensures efficient degreasing. Upon reducing the salt mass fraction the phase behaviour shifts to higher temperatures. At the degreasing temperature now an oil-in-water microemulsion coexists with an oil-excess phase. Shearing induces the formation of a stable macroemulsion that prevents the depositing of the fat on the skin and ensures the transport of the fat away from the skin. Note that only the Gibbs triangles correspond to the real experimental conditions. The T - γ cuts are shown for clarity.

groups increases and the surfactant becomes effectively more hydrophilic [3]. As a result the phase behaviour shifts to higher temperatures as shown in Fig. 10.12(b) [166–169]. At the degreasing temperature $T = 30^\circ\text{C}$, the system is now in the phase state $\underline{2}$, where an o/w microemulsion coexists with an oil excess phase. Shearing induces the formation of a stable macroemulsion, which prevents the fat from depositing on the skin and enables the transport of the fat away from the skin.

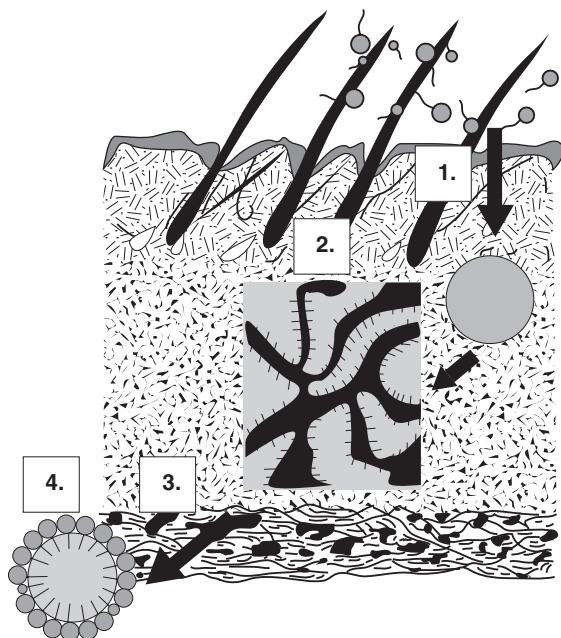


Figure 10.13 Schematic of the four-step process of degreasing according to the interplay of micro- and macroemulsions. (From Ref. [171], reprinted with permission of Umschau Verlag.)

10.4.3 The degreasing mechanism

Efficient degreasing was found to be closely connected to the three-phase state and hence to the ultra-low interfacial tension between water and oil [170]. The so far unidentified mechanism of degreasing of animal skins could be understood and explained. Correlation of results obtained from phase behaviour measurements and degreasing experiments revealed that Eusapon[®]OD shows the best degreasing performance and lead to the clarification of the four-step process of degreasing as shown in Fig. 10.13 [171]. The first step is the penetration of the surfactant into the skin. In a second step the natural fat is solubilised. A microemulsion phase coexists with a fat- and a water-excess phase and the interfacial tension between water and oil is ultra-low. On the surface of the skin dilution of the microemulsion with pure water, i.e. reduction of the salt concentration in the float, leads to the formation of a stable emulsion via shearing. The stable emulsion prevents the deposition of the fat on the skin and enables the transport of the natural fat away from the skin.

Acknowledgement

SE would like to thank for the performance of the degreasing experiments in the BASF beam house.

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