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Feature Article

Liquid crystalline surfactant phases in chemical applications

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The importance of lyotropic liquid crystalline structures is shown for two selected surfactant applications, *i.e.* cosmetics and detergency. The properties of lyotropic liquid crystals are demonstrated for binary surfactant–water systems, ternary surfactant–oil–water systems and multicomponent systems. Detailed knowledge of the phase behavior is crucial for tailor-made product development.

1 Introduction

Liquid crystalline structures have received a good deal of attention in recent years. Besides being used in the scientific study of cooperative phenomena and complex fluid phases these structures have found applications in electrooptic displays, sensors, optical switches and shutters, and thermography. The liquid crystalline structures formed by amphiphilic molecules form the basis for emulsions and have been studied thoroughly by researchers in the food, drug, oil and chemical industries.

Two different types of structures have been distinguished: thermotropic liquid crystals and lyotropic liquid crystals. Although lyotropic phases have not been given the same prominence as thermotropic phases, their importance should not be underestimated. The phases are crucial in the manufacture and mode of operation of detergents and have an important role in cosmetics. In lyotropic systems, the transition from one phase to another can occur owing to the change of concentration. Of course temperature can also cause phase transitions in these systems, so this aspect of thermotropic liquid crystals is shared by lyotropics. The real distinctiveness of lyotropic liquid crystals is the fact that at least two different species of molecules (*e.g.* solute and solvent) must be present for these structures to form.

The following review will summarize basic principles of lyotropic liquid crystalline phases using specific applications in cosmetics and detergency. Of course the results can be transferred to other applications.

2 Cosmetic applications

In the field of cosmetics, surfactants are widely used as wetting agents, emulsifiers and/or stabilizers. Cosmetic products can be regarded as belonging to either one of the two following categories: surfactant + solvent (water or oil) or surfactant + oil + solvent. In most of the cases cosmetic products are based on water being the solvent and lyotropic liquid crystals as the predominating structures providing the specific properties of the product.

Typical cosmetic products of the first category are hair and body shampoos or shower gels, facial cleansers and toothpastes. All these products have in common the fact that the presence of liquid-crystalline surfactant phases is induced in order to provide appropriate rheological properties. In particular, lamellar liquid crystals are preferred since their bulk viscosities are not as high as those of hexagonal or cubic liquid crystals and the shear thinning effect in these systems is convenient during application. Of course other means to adjust product rheology are common, *e.g.* addition of polymers or salt-induced micelle-to-rod transitions for low concentrated formulations. Furthermore cosmetic products with definite viscosities are able to incorporate additives which at much lower viscosities would segregate out of the product, *i.e.* pearlescent agents in hair shampoos.

In ternary systems composed of water, surfactants and oils or hydrocarbons the presence of liquid crystals has a major impact on system properties such as microscopic structure, viscosity, stability and foaming performance.

Stabilization of foams

The foaming ability of, for example, oil continuous solutions is dependent on the phase behavior of the system.[1] On the surfactant and hydrocarbon rich side of the phase diagram (Fig. 1, black area) two different phases can be distinguished.

In the L-phase (w/o emulsion) as well as the LC phase (liquid crystal) foam lifetimes were only of the order of seconds. On the other hand, in the two-phase region (hatched area) foam lifetimes increased up to several hours indicating that the presence of a liquid crystal enhances and stabilizes the foam. This stabilization effect can be attributed to the influence of the liquid crystal on the foam drainage. Microscopic pictures using polarized light[2] reveal that the liquid crystals concentrate in the plateau borders of the foam where its high viscosity reduces the drainage of the foam considerably. For this reason the plateau borders and the radii of its curvature remain large causing the Laplace pressures and the thinning rates of the foam lamellae to be small.

In addition, the surfactants in the liquid crystalline phase result in lower surface tensions and hence higher surface pressures in the foam lamellae compared to the situation where only surfactants are present. In this respect the liquid crystals

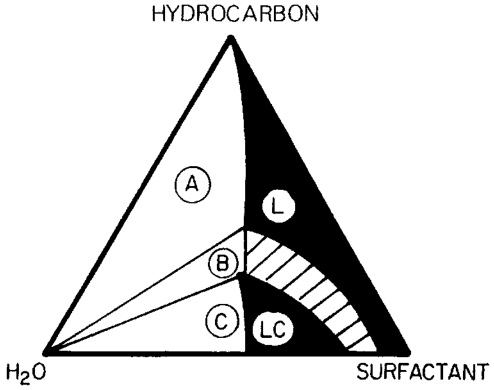

Fig. 1 Phase diagram of water–hydrocarbon–oil-soluble surfactant forming foams only in the two-phase area L + LC (reproduced with permission from ref. 1; for explanation of abbreviations see text)

in the plateau border serve as a surfactant reservoir of optimum composition for the stabilization of the foam films.

Stabilization of emulsions and dispersions

The application of lamellar liquid crystalline phases for the stabilization of emulsions has been reported by Friberg *et al.*[3] Emulsions or dispersions can be further stabilized by crystallization of lamellar liquid crystalline phases located at the water/oil interface resulting in the formation of a so-called gel phase.[4–6]

We have demonstrated[6] that changes in the type and concentration of the co-emulsifier caused the formation of a lamellar gel phase surrounding the oil droplets inside an oil-in-water (o/w) emulsion which increased the stability of the emulsion from 5 days (emulsion 1) to more than 1 month (emulsion 2; see Table 1 and Fig. 2). Great care was taken to make sure that the physico-chemical properties of the system remained unaffected by the change of the co-emulsifier. In Table 1 the viscosities and the phase inversion temperatures (PIT) are compiled together with the particle size distributions of the two emulsions. The data suggest that only the presence of the lamellar liquid crystalline phase causes the observed increase in emulsion stability.

The viscous lamellar film surrounding the emulsion droplets may be several layers thick and reduces the attraction potential between the droplets [see Fig. 2(*c*)].[7,8] As a result, the lamellar layer acts as a barrier against coalescence.

Friberg[9] distinguished between emulsions or two-phase systems being stabilized by a monomolecular surfactant layer at the interface between oil and water and three-phase emulsions with regular structures of multimolecular layers that can be regarded as a distinct phase which can exist independently from the emulsion, *e.g.* after separation by centrifugation. Emulsions containing a third phase or multimolecular layers of lyotropic liquid crystals are often found in cosmetic products (Fig. 3) and is therefore widely used by the cosmetics industry to adjust or optimize specific properties of the product such as viscosity or consistency, storage stability or application convenience.

Fig. 3 shows a conventional and a polarization microscope picture of a commercial hand lotion with a liquid crystal present at the interface between the oil droplets and the continuous water phase. The liquid crystal is assumed to consist of multiple layers or shells stabilizing the dispersed phase (see Fig. 4).

These kinds of three-phase emulsions can be found in cosmetic products ranging from lotions to creamy emulsions and are believed also to exist in food products in which lecithin and monoglycerides are commonly used as emulsifiers.[10,11]

Table 1 PIT emulsion systems (% by mass of active substance)

	emulsion concentrate		final formulation	
component/property	1	2	1	2
$C_{16/18}E_{12}$	5.7	8.0	2.7	3.8
glyceryl monostearate	—	5.0	—	2.4
$C_{12/14}E_4$[a]	7.3	—	3.5	—
dicapryl ether	42.0	42.0	20.0	20.0
water	45.0	45.0	73.8	73.8
PIT/°C	73.4	74.0	—	—
viscosity/mPa	300	300	30	36
mean particle size[b]/nm				
fresh	—	—	350	305
aged	—	—	3500	450
mean particle size[c]/μm				
fresh	—	—	<1	<1
aged	—	—	2.7	<1

[a]Narrow range ethoxylate. [b]Zetasizer, Malvern. [c]By light microscopy (from ref. 6).

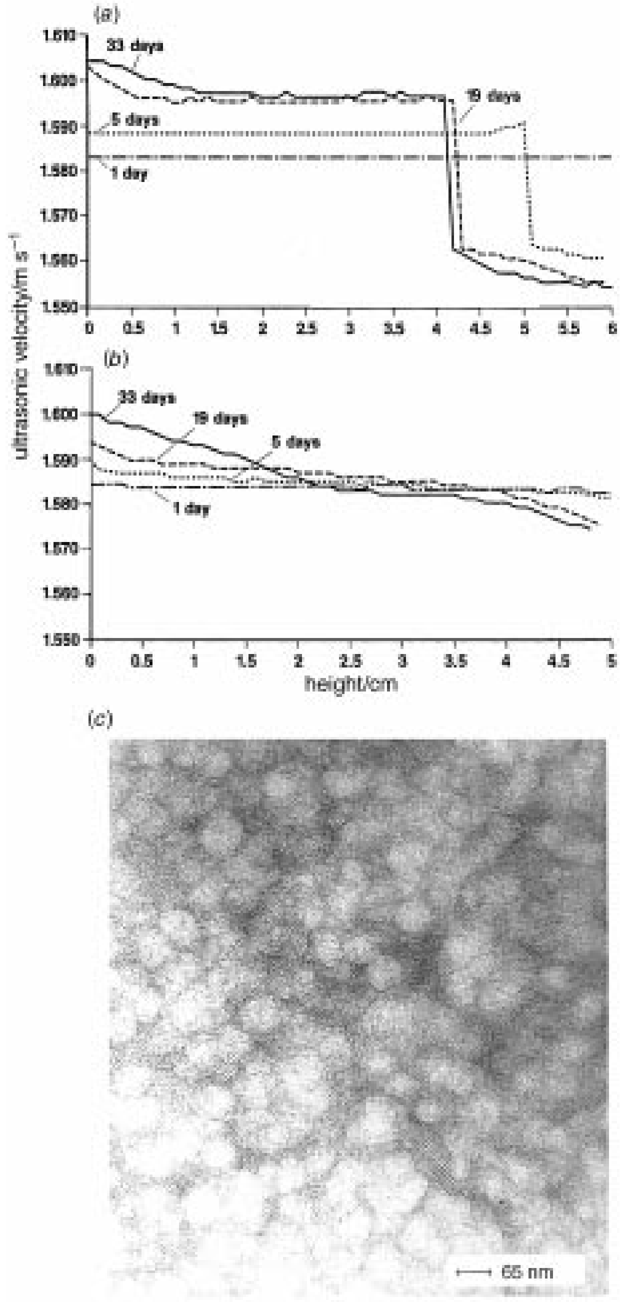

Fig. 2 Influence of co-emulsifier type on emulsion stability. Ultrasonic density scans of the vessel containing emulsions 1 (*a*) and 2 (*b*); (*c*) TEM image of emulsion 2 containing liquid-crystalline gel phases stabilizing the oil droplets (reproduced with permission from ref. 6).

Networks formed by liquid crystals

Similar to the effect of polymer additives, liquid crystalline phases are capable of forming three-dimensional networks extending through the continuous phase of the system. Like polymer thickeners the network reduces the Brownian motion of the dispersed particles or droplets and thus add to the stability of the system (see Fig. 5).

In the field of pharmacology rigid network structures made up of liquid crystalline structures may dissolve substances that otherwise show only limited solubility. Wahlgren *et al.*[13] demonstrated that the solubility of hydrocortisone in isotropic solvents is small, *ca.* 1.5% in ethylene glycol, whereas in a lamellar liquid crystalline phase of lecithin and water the solubility exceeds 4%.

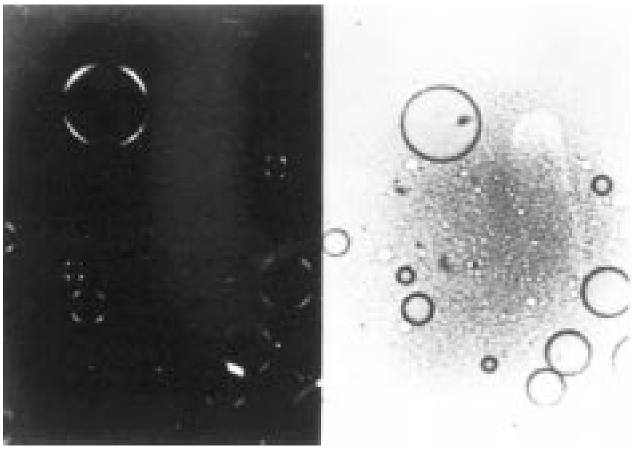

Fig. 3 Liquid crystals in a hand lotion visualized using polarized light microscopy (reproduced with permission from ref. 9)

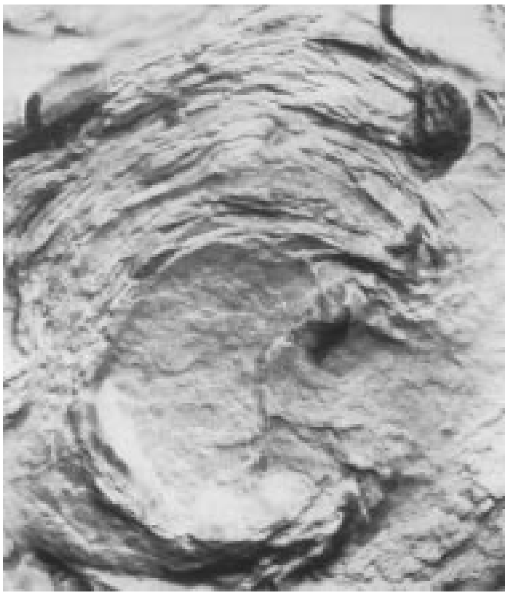

Fig. 4 Electron microscope image of freeze-fracture of liquid crystalline layers in an emulsion (reproduced with permission from ref. 9)

Liposomes

Liposomes are supramolecular structures or vesicles of mono-(uni-) or multilamellar surfactant bilayers with a hollow core which can be regarded as an intermediate structure between micelles (surfactant monolayer on the surface of an imaginary sphere) and lamellar liquid crystals (plane bilayers). In a way liposomes can also be regarded as lamellar liquid bilayers which have transformed by bending and have fused to a closed spherical shell. They are usually discussed in terms of controlled release and specific drug targeting in the fields of pharmacology, cosmetics, food industry and agrochemicals.[14–16]

With respect to controlled drug release a delayed delivery because of low diffusion coefficients for the solubilized drugs *via* vesicles or liposomes incorporating, for example, insulin is discussed.[17,18]

Specific drug targeting is aimed at by designing vesicles binding to cells with high selectivities and affinity; *e.g.* immunoliposomes bearing ligands (*e.g.* antibodies) that are recognized by specific cell receptors.[19,20]

Liquid crystals in emulsification processes

The mixing of at least two mutually insoluble liquid phases is usually referred to as emulsification or dispersion.[21] The process itself involves the creation of large interfacial areas between the dispersed and continuous phase which requires the energy $A\gamma$ (internal surface $A \times$ interfacial tension $\gamma_{o/w}$) and thus renders the emulsion thermodynamically metastable or even unstable. The addition of surfactants which reduce the interfacial tension $\gamma_{o/w}$, or the presence of liquid crystals which prevent the phase separation, *i.e.* the decrease of the total energy of the system towards the thermodynamic equilibrium, by modifying the rheological properties of the system, are the two main concepts to stabilize emulsions usually of either oil-in-water (o/w) or water-in-oil (w/o) types. However, for cosmetic and technical applications, microemulsions with even higher interfacial areas, but being thermodynamically stable, and multiphase emulsions, *e.g.* of the w/o/w type, are quite common too. In the case of microemulsions the considerable amount of positive entropy of mixing over-compensates the amount of interfacial energy required to form the microemulsion which on the other hand has been minimized because of an extreme reduction of the interfacial tension due to an optimal match of emulsifier and oil properties.

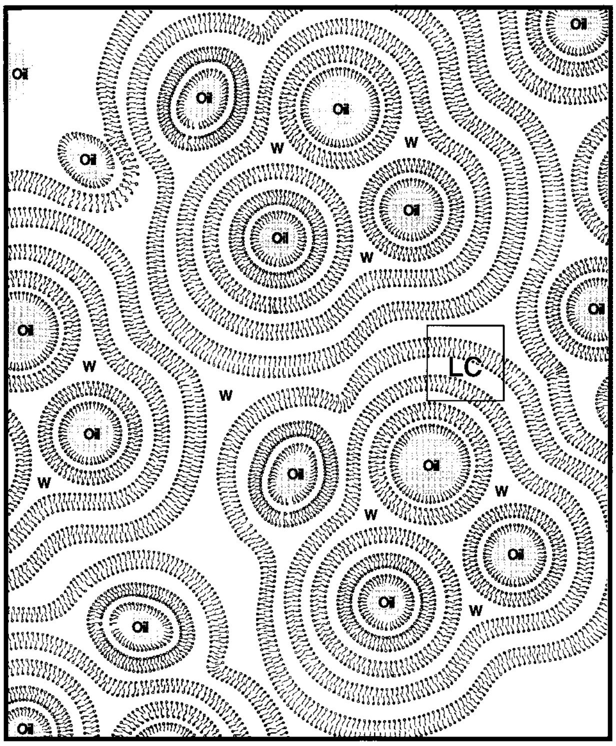

Fig. 5 Three-dimensional network structure of oil/liquid crystal/water emulsions (reproduced with permission from ref. 12)

The stabilization effects of surfactants on emulsions are due to their amphiphilic molecular structure with hydrophilic and lipophilic moieties. The tendency to accumulate at interfaces resulting in the reduction of interfacial energies and to aggregate in aqueous solutions forming thermodynamically stable micellar structures or lyotropic liquid crystals offers possibilities for changing the macroscopic appearance and properties of emulsions.

The presence of liquid crystalline structures during the formation or production of technical or cosmetic emulsions is of paramount importance for the PIT, as well as the gel-phase emulsification.

PIT- emulsification

The above mentioned optimized balance between the amphiphilic properties of the emulsifier system with the hydrophobicity of the oil phase and the hydrophilicity of the water phase, being modified by the presence of salts or water soluble components of the oil phase, represents the essential part of the PIT emulsification process resulting in the extreme fine dispersity of the emulsion which is necessary, for example, for the required long-term stability during storage.

The phase-inversion temperature (PIT) emulsification has been developed for emulsions based on ethoxylated fatty alcohol nonionic surfactants and requires a heating–cooling cycle[22,23] (see Fig. 6).

Starting at ambient temperatures with a coarsely dispersed o/w emulsion upon temperature increase the system passes through a microemulsion or bicontinuous lamellar phase at the PIT resulting in the formation of a w/o emulsion at temperatures exceeding the PIT-range. The temperature induced inversion effect is related to the clouding phenomenon of the ethoxylated nonionic surfactants which change their solubilization properties with increasing temperature. The clouding phenomenon finally leads to a separation of the system into two phases, one of which is a dilute surfactant phase whereas the other phase consists of a concentrated micellar solution in thermodynamic equilibrium with the dilute phase. The effect is ascribed to a temperature dependent change of the hydration of the ethylene oxide groups of the hydrophilic headgroup of the nonionic surfactant. At higher temperatures the intermolecular interactions between water and the surfactant head group are less energetically favorable than the interaction between water or the nonionic molecules themselves.

During the PIT-process upon reduction of the temperature the system re-inverts from the w/o emulsion to an o/w emulsion causing a simultaneous break-up of the planar or bicontinuous intermediate phase into a multitude of spherical oily droplets of extreme fine dispersity with only minimal mechanical energy required. The extreme fine dispersity is the reason why PIT-emulsions exhibit much longer shelflives than emulsions with more coarsely distributed particle sizes.

Gel-phase emulsification

Another way to produce finely dispersed emulsions associated with a change in the hydrophilic/lipophilic balance is called gel-phase emulsification (Fig. 7). In this two-stage process a microemulsion or a lamellar gel phase is induced through an additional component which modifies the hydrophilic/lipophilic properties of the solvent, *e.g.* addition of a polyol to water.[24–26] By proper choice of this additive and the surfactant as well as optimization of their relative ratio the gel-phase emulsification can be adapted to different oils. The whole process can be operated at a definite temperature, *e.g.* at room temperature.

In the first step the oil phase is dispersed in a lamellar phase. In this particular case the lamellar phase consists of surfactant (monoarginine hexyldecyl phosphate), polyol (glycerol) and a small amount of water. Oil phase (o) and lamellar phase (lc) together form a transparent o/lc gel phase. In contrast to the PIT-process the gel-phase emulsification does not require a definite type of surfactant. The surfactant may be anionic or nonionic.

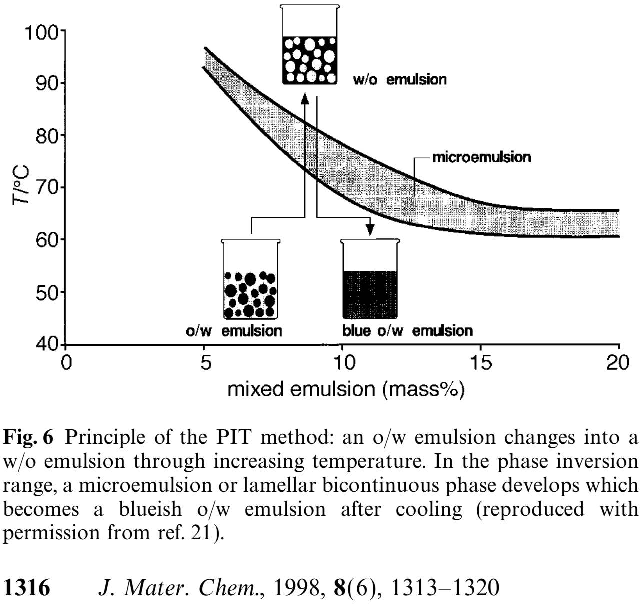

Fig. 6 Principle of the PIT method: an o/w emulsion changes into a w/o emulsion through increasing temperature. In the phase inversion range, a microemulsion or lamellar bicontinuous phase develops which becomes a blueish o/w emulsion after cooling (reproduced with permission from ref. 21).

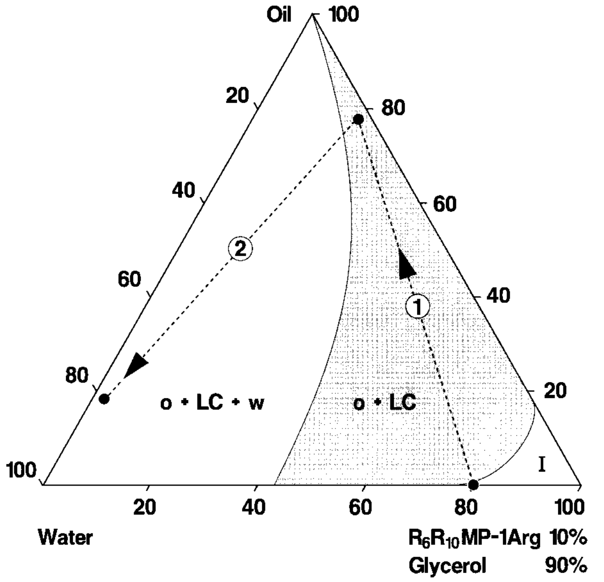

Fig. 7 Principle of the gel-phase emulsification (reproduced with permission from ref. 25): 1, formation of an o/lc gel emulsion containing oil (o), monoarginine hexyl decyl phosphate (R_6R_{10}MP-1Arg), glycerol and a small amount of water (w) (lc = lamellar phase); 2, dilution of the o/lc emulsion with cold water

In the second step the o/lc gel is diluted with a definite amount of water to form the final o/lc/w emulsion. In this emulsion the presence of the lamellar liquid crystalline phase protects the oil droplets against coalescence (like in ref. 6).

The particle size distribution of the dispersed oil droplets is primarily dependent on the surfactant/oil ratio and can be adjusted to cover the whole range from less than 100 nm to even more than 1000 nm. Thus together with the PIT-process the gel-phase emulsification offers the opportunity to produce finely dispersed o/w emulsions for the use in the cosmetics industry in a simple and cost-saving way which satisfies the fundamental requirements of long shelflives and stability against coalescence.

Structure of the epidermis

So far liquid crystalline structures have been discussed merely in the sense that they affect the structure and stability of oil and/or water-based products. But apart from that they are an essential part of the human epidermis (Fig. 8).[27–29] During the cell differentiation from the lower parts of the epidermis (*stratum basale*) to the upper parts (*stratum corneum*) the chemical composition of the lipids of the skin change. The *stratum basale* is mainly composed of phospholipids and small amounts of cholesterol, ceramides and fatty acids (malpighian cells). In the granular cells of the intermediate *stratum granulosum* nearly equal amounts of phospholipids, cholesterol, ceramides and fatty acids can be found. The formation of lamellar liquid crystalline structures in the human skin requires a minimum amount of fatty acids. Together with the skin lipids these lamellar structures are stored in the granules of the *stratum granulosum*. Between the horny cells of the *stratum corneum* these granules fuse to form lamellar lipid membranes and thus constitute an epidermal barrier against water loss. The skin lipids of the *stratum corneum* are mainly composed of fatty acids, cholesterol and ceramides which together determine the properties of this water barrier. Knowledge of the

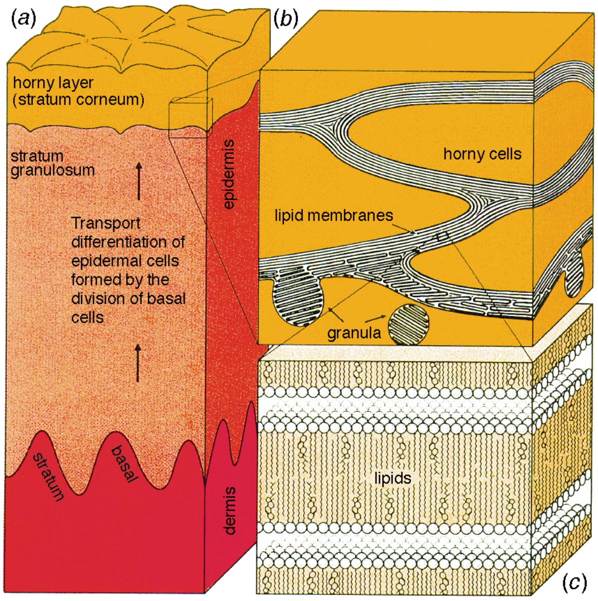

Fig. 8 Epidermal structure of the human skin. Schematic representation of the horny layer (*a*) and the lipid barrier (*b*, *c*). Lipids are formed during cell differentiation and stored in granula as disks, which are released into the intracellular space during transfer to the horny layer (*b*). There they fuse into 'endless' lipid membranes (*c*) which are water impermeable. (Reproduced with permission from ref. 30.)

structural and chemical composition of the human epidermis can be taken advantage of in cosmetic products. The repair of the lamellar structures in the epidermis or the supply of essential fatty acids or ceramides should result in a well developed skin barrier. As a consequence the reduction in trans-epidermal water loss increases the water content of the upper skin and wrinkle formation should be significantly reduced.

3 Lyotropic liquid crystals in detergency

Detergent performance

Nonionic surfactants of the alkylpolyglycol ether type are key ingredients of detergent formulations because of their good detergency properties.[31] The interfacial and colloidal properties of alkylpolyglycol ethers have been the subject of numerous publications. In particular, the phase behavior of binary mixtures of water and nonionic surfactants has been intensively investigated.[32,33] Besides molecular, micellar and inverse-micellar solutions, single and two-phase liquid crystal regions, as well as 'anomalous' phases, have been observed. Apart from these binary mixtures, ternary systems of the water/surfactant/oil type have also been studied. These mixtures may form three-phase microemulsions that are of interest with regard to special applications, since extremely low interfacial tensions exist between the single phases.[34] Generally, interfacial tension is the restraining force regarding removal of liquid oil from a solid surface[35] and in the displacement of oil from narrow capillaries, as is the case with enhanced oil recovery.

At the surfactant solution/oil or the surfactant solution/fat interface, liquid crystals may be formed by penetration of surfactant molecules. Model experiments have shown that the formation of mesophases strongly affects detergency.[36–38] Beside this effect liquid crystalline phases are of equal importance for the formulation of liquid products.

The phase behavior of nonionic surfactants with a low degree of ethoxylation is very complex. As the lower cosolute boundary is shifted to lower temperatures with decreasing EO (ethylene oxide) number of the molecule, an overlapping of this boundary with a mesophase region may result, as depicted in Fig. 9. At low surfactant concentrations in such systems, several two-phase areas are observed in addition to the single-phase isotropic L_1 range: two coexisting liquid phases ($W+L_1$), a dispersion of liquid crystals ($W+L_\alpha$) and a two-phase region of water and a surfactant liquid phase ($W+L_2$).

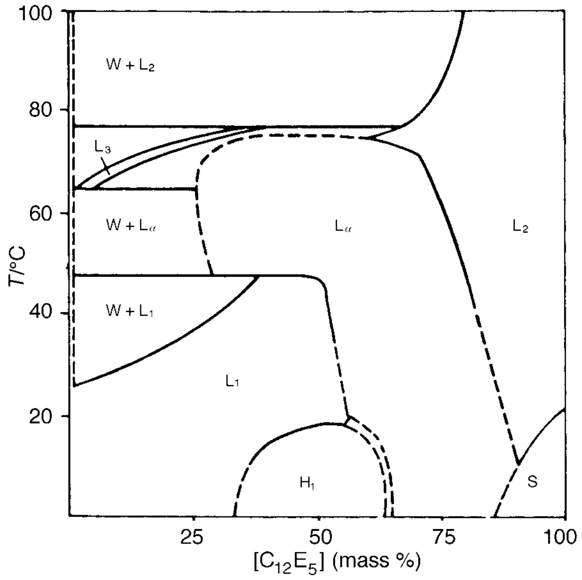

Fig. 9 Phase diagram of the binary system water–pentaoxyethylene *n*-dodecanol ($C_{12}E_5$) (reproduced with permission from ref. 33)

In ternary mixtures of water, surfactant and oil, three phases may coexist in equilibrium. These systems are also referred to as three-phase microemulsions. When these three phases are formed, extremely low interfacial tensions between two phases are observed. Because the interfacial tension is generally the restraining force, with respect to the removal of liquid soil in the washing and cleaning process, it should be as low as possible for optimal soil removal. Other quantities such as the wetting energy and the contact angle on polyester, as well as the emulsifying ability of *e.g.* olive oil, also show optima at the same mixing ratio at which the minimum interfacial tension is observed.[39]

Fig. 10 (right) represents the three-phase temperature intervals for $C_{12}E_4$ and $C_{12}E_5$ *vs.* the number (*n*) of carbon atoms of *n*-alkanes.[40] Both parts of Fig. 10 indicate that the maximum oil removal is in the three-phase interval of the oil used (*n*-hexadecane). This means that not only the solubilization capacity of the concentrated surfactant phase, but probably also the minimum interfacial tension existing in the range of the three-phase body are responsible for the maximum oil removal.

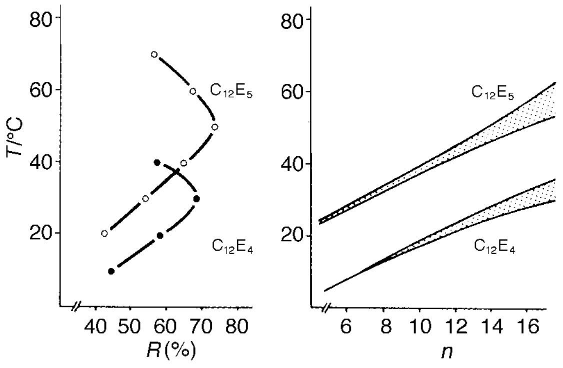

Fig. 10 Phase behavior of the polyoxyethylene alcohols $C_{12}E_4$ and $C_{12}E_5$, and detergency:[40] three-phase temperatures *versus* number *n* of carbon atoms (right) and detergency (*R*) as a function of temperature (left) (reproduced with permission from ref. 42)

Tests with pure low ethoxylated surfactants have shown that a discontinuity is observed with respect to oil removal *versus* temperature in cases of the existence of dispersions of liquid crystals in the binary system water/surfactant. Fig. 11 shows that the detergency values for mineral oil and olive oil, *i.e.* two oils with significantly different polarities, are at different levels. It also shows that in both cases a similar reflectance *vs.* temperature curve exists. In the region of the liquid crystal dispersion, *i.e.* between 20 °C and 40 °C, the oil removal increases significantly. Above the phase transition $W+L_\alpha \rightarrow W+L_3$, between 40 °C and 70 °C, no further increase in oil removal takes place. For olive oil, a small decrease in detergent performance is observed. The interfacial tensions between aqueous solutions of $C_{12}E_3$ and mineral oil lie at about $5\,mN\,m^{-1}$ at 30 °C and 50 °C. These relatively high values indicate that in this system the interfacial activity is not the decisive factor in oil removal from fabrics.

In the case of $C_{10}E_4$, which is substantially more hydrophilic than $C_{12}E_3$ (Fig. 11), a phase transition of the two co-existing liquid phases into a liquid crystal dispersion takes place in the temperature range investigated. Here, too, the reflectance greatly increases above the phase transition temperature in the region where the liquid crystal dispersion exists. Whereas an interfacial tension of $0.3\,mN\,m^{-1}$ occurs at 40 °C, a value approximately ten times higher is observed at 60 °C. Thus, the interfacial tension increases with increasing temperature in this ternary mixture. The strong increase of reflectance cannot, therefore, be attributed to the increase of the amount of surfactants adsorbed, which would manifest itself in a decrease in the interfacial tension.

In both the examples, neither the position of the cloud point nor the existence of a three-phase body are responsible for the strong temperature dependence of oil removal. Rather, the macroscopic properties of the liquid crystal dispersion seem to be responsible for the strong temperature dependence. It can be assumed that fragments of liquid crystals are adsorbed onto fabric and oily soil in the $W+L_\alpha$ range during washing. The local surfactant concentration is therefore substantially higher in comparison to the monomolecular surfactant layer that forms when surfactant monomers adsorb. As the viscosity of liquid crystals in the single-phase range is strongly temperature dependent,[41] it can be assumed that the viscosity of a fragment of a liquid crystal deposited on a fabric also significantly decreases with increasing temperature. Thus, the penetration of surfactant into the oil phase and removal of oily soil are promoted.

Apart from pure nonionic surfactants, technical grade surfactants are of specific interest for applications. As in the case of pure nonionic surfactants, definite ranges exist in which there is only a slight dependence of oil removal on the temperature (Fig. 12). For $C_{12-18}E_{\bar{5}}$, this is in the range of the two co-existing liquid phases ($W+L_1$) and for $C_{12-18}E_{\bar{4}}$ it is in the range of the surfactant liquid phase ($W+L_2$). An unusually strong increase of oil removal with increasing temperature occurs in the region of the liquid crystal dispersion ($W+L_\alpha$). At 30 °C and 50 °C, the interfacial tensions between aqueous surfactant solutions and mineral oil and the contact angle on glass and polyester were determined for $C_{12-18}E_{\bar{4}}$. Whereas the values of the interfacial tensions are practically identical (approximately $10^{-1}\,mN\,m^{-1}$ after 15 min), the contact angles on both substrates are slightly less advantageous at higher temperature. Hence, the increased oil removal between 30 °C and 50 °C cannot be attributed to an increase in the adsorbed amounts of surfactants. Rather, in both cases, the decisive part is probably played by the macroscopic properties of the liquid crystal dispersion and their temperature dependence.

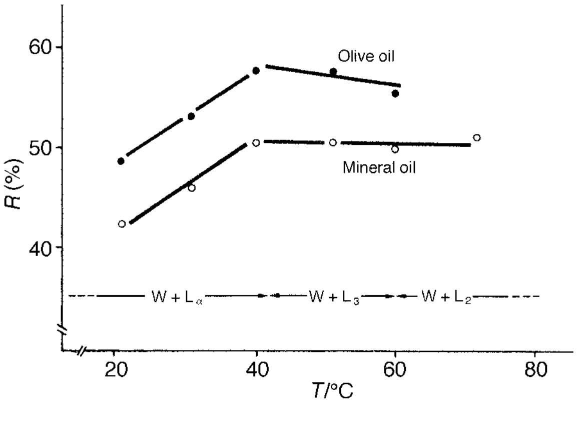

Fig. 11 Phase behavior of the polyoxyethylene alcohol $C_{12}E_3$ and detergency (2 $g\,l^{-1}$ surfactant) (reproduced with permission from ref. 42)

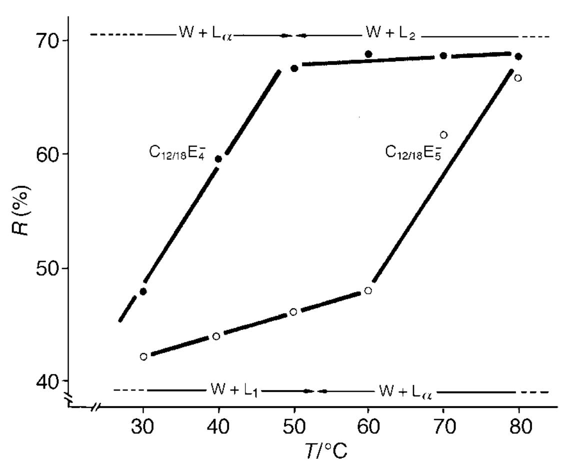

Fig. 12 Phase behavior of the polyoxyethylene alcohols $C_{12/18}E_4$ and $C_{12/18}E_5$ and detergency. The line above the number of the oxyethylene groups indicates that it is a mean value (reproduced with permission from ref. 42).

Flow behavior

Besides detergency the liquid crystalline phases of surfactant systems at higher concentrations are of crucial importance for the processing of concentrated surfactant systems and the formulation and application of liquid products. In such cases not only the phase behavior but also the rheological properties are of interest for the user. Characteristic properties of surfactant systems will be shown in the following examples for different types of nonionic surfactants.

Alkyl polyglycosides form a new class of surfactant, which show favourable physical chemical properties.[43] The phase behavior of a technical $C_{8/10}$-alkyl polyglycoside ($C_{8/10}$-APG) is illustrated in Fig. 13.[44] At temperatures above 20 °C, the $C_{8/10}$-APG is present up to very high concentrations in an isotropic phase, the viscosity of which increases considerably.

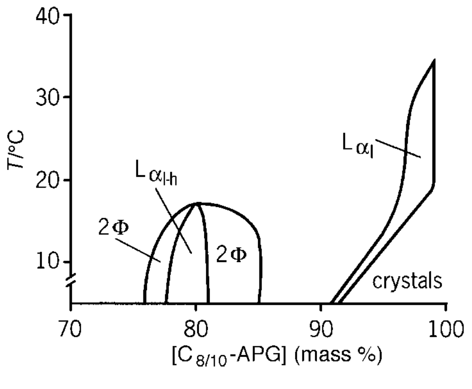

Fig. 13 Phase diagram of the $C_{8/10}$-APG/water system (2Φ = two-phase region) (reproduced with permission from ref. 44)

A birefringent lyotropic phase of nematic texture is formed at around 95% by mass, which changes at around 98% by mass into a cloudy two-phase region of liquid and solid alkyl polyglycoside. At relatively low temperatures, a lamellar liquid crystalline phase is additionally observed between 75 and 85% by mass.

The phase diagram of the $C_{12/14}$-alkyl polyglycoside ($C_{12/14}$-APG)/water system (Fig. 14) differs clearly from that of the short-chain APG. At low temperatures, a region resembling a solid/liquid system below the Krafft point is formed over a wide concentration range. With an increase in temperature, the system changes into an isotropic liquid phase. Since crystallization is kinetically retarded to a considerable extent, this phase boundary changes position with the storage time. At low concentrations, the isotropic liquid phase changes above 35 °C into a two-phase region of two liquid phases, as is normally observed with nonionic surfactants.[45] At concentrations above 60% by mass, a sequence of liquid crystalline phases is formed at all temperatures examined. It is important to mention that, in the isotropic single-phase region, a distinct streaming birefringence can be observed at concentrations just below the lyotropic phases, disappearing again rapidly on completion of the shearing process. However, no multiphase regions separating this region from the L_1 phase could be found. In the dilute L_1 phase, there is another region with weaker streaming birefringence which is situated near the minimum of the liquid/liquid miscibility gap. The rheological properties of highly concentrated alkyl polyglycoside systems are summarized in ref. 42.

Paasch *et al.* studied the rheological properties of lamellar liquid crystalline phases of alkyl polyethylene glycol ethers.[46] The rheological measurements of lamellar liquid crystals indicate that the phases studied are, without exception, plastic systems. As an example, flow curves obtained from measurements of $C_{12}E_4$, 60% by mass, are reproduced in Fig. 15. The first measurement on the ascending curve indicates a clearly higher yield value than is given by the descending curve. When the measurements are repeated, the yield value on the ascending curve corresponds to that on the first descending curve. This suggests that an orientation of the anisotropic phases took place in the shear field when they were first subjected to shear stress. The lower yield value obtained when the measurements were repeated corresponds to that of the aligned sample.

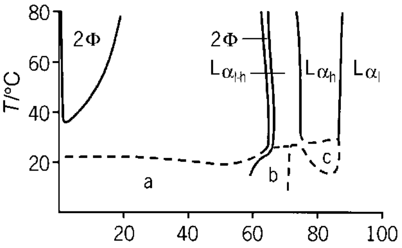

Fig. 14 Phase diagram of the $C_{12/14}$-APG/water system (a, b and c indicate crystalline precipitates or liquid crystalline phases) (reproduced with permission from ref. 44)

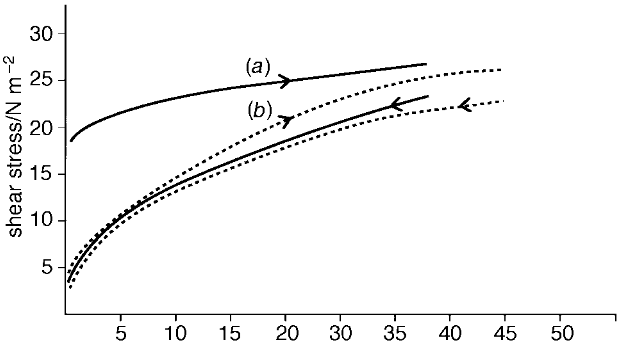

Fig. 15 Flow curves of the polyoxyethylene alcohol $C_{12}E_4$ (60 mass%)–water system: (*a*) first measurement; (*b*) repeat measurement (reproduced with permission from ref. 46)

Fig. 16 shows the yield value given by the ascending and descending curves for $C_{10}E_4$ as a function of the surfactant concentration. When first subjected to shear stress, the samples gave yield values up to 80 Pa; when the measurements were repeated, these values sank below 20 Pa. The yield value increases with the surfactant content of the lamellar phase, only to decrease rapidly in the two-phase region $L_\alpha + L_2$. Before the first measurements are taken, the orientation of the anisotropic phases is not defined. Therefore, their rheological properties vary distinctly. This is not the case with the oriented samples; there is scarcely any recognizable concentration dependence; the yield values are around 10 Pa.

Similar results are obtained for the shear viscosity as a function of concentration. For the freshly produced samples not previously subjected to shear stress, the viscosity increases systematically as the concentration of the surfactant is increased. After being subjected to shear stress, the samples show distinctly smaller variations in viscosity when the measurements are repeated. This also suggests that the viscous flow of the oriented samples occurs by sliding of layers whose properties are barely affected by the concentration.

Fig. 17 shows the yield values of samples of the same composition (10 mol%), obtained from the ascending curve, as a function of EO and alkyl chain length. As the EO number increases, the yield value increases by about 10 Pa in the case of C_{12} ethoxylates and about 5 Pa in the case of C_{10} surfactants. The value for the C_{10}-polyethylene glycol ethers is higher than

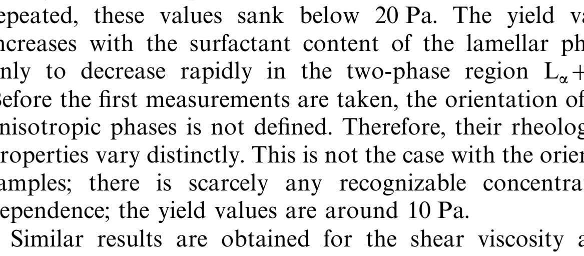

Fig. 16 Yield values of the polyoxyethylene alcohol (C_{10}4EO)–water (*w*) system (up = ascending curve, down = descending curve) (reproduced with permission from ref. 46)

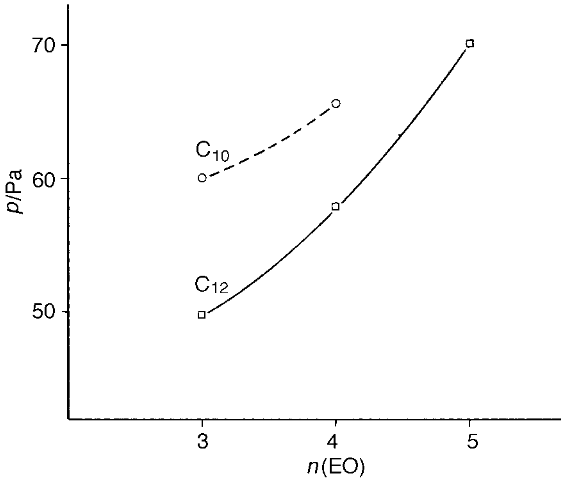

Fig. 17 Yield values given by the ascending curves as a function of the length of the alkyl chain and the number of oxyethylene groups *n* (EO) (concentration = 10 mol%) (reproduced with permission from ref. 46)

the values of the C_{12}-ethoxylates; this is probably a result of the higher proportion of EO chains in the molecule. The same relationship holds true at different concentrations.

In contrast, the yield values of the oriented samples at a surfactant concentration of 10 mol% show no dependence on the type of surfactant. The liquid crystals formed from the various surfactants all have roughly the same value of approximately 10 Pa. This is surprising, since the lengths of the polyethylene glycol and alkyl chains apparently have no influence on the plastic properties of the oriented liquid crystals. These aspects must be considered for the handling of such fluids in technological processes and consumer products.

4 Outlook

The importance of liquid crystalline structures has been shown for two selected surfactant applications, *i.e.* cosmetics and detergency. The demonstrated basic principles of liquid crystals which are needed for the optimization of product properties are of course valid in other application fields as well. For each application where surfactants are part of a product detailed knowledge has to be gathered about how to cope with the special properties of liquid crystals.

The generation, incorporation or modification of liquid crystalline structures are the daily challenges of product development in order to optimize the products. Further efforts are still needed to transfer and apply fundamental knowledge to more application oriented problems concerning the tailoring of liquid crystal-based products to specific market or customer demands.

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