Journal of Colloid and Interface Science 364 (2011) 148–156

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Solubilisation of different medium chain esters in zwitterionic surfactant solutions – Effects on phase behaviour and structure

A. Barth [a], S. Prévost [a,b], J. Popig [a], M. Dzionara [a], G. Hedicke [a], M. Gradzielski [a,*]

[a] Stranski-Laboratorium für Physikalische und Theoretische Chemie, Institut für Chemie, Technische Universität Berlin, D-10587 Berlin, Germany
[b] Helmholtz-Zentrum Berlin, Lise-Meitner Campus, D-14109 Berlin, Germany

ARTICLE INFO

Article history:
Received 16 March 2011
Accepted 28 June 2011
Available online 12 August 2011

Keywords:
Zwitterionic surfactant
Ester
Cosurfactant
Phase diagram
SANS

ABSTRACT

We studied the effect of solubilisation of methyl esters with different chains of medium length into the binary surfactant system tetradecyldimethylamine oxide/water at constant surfactant concentration of 200 mM. As esters we employed valeric, capronic, enanthic, and pelargonic methyl ester, thereby decreasing the polarity. Always a phase sequence L_1–L_α–L_1 is observed with increasing ester concentration, where the L_α-phase increases in extent and goes to much lower temperatures with increasing chain length of the ester. Viscosity measurements show a maximum at intermediate concentrations of additive that is independent of the type of ester. From SANS measurements detailed information about the structural changes occurring during the rod-to-sphere transition in the system of the shortest additive is deduced, which proceeds first through a pronounced rod growth. Interestingly, for the different esters an almost constant value of the volumic solubilisation capacity is observed, in agreement with the relatively constant interfacial tension. For the different esters no effect on the radius and the area requirement at the amphiphilic interface is observed at the solubilisation boundary. The microemulsions present here are spherical aggregates where the ester is partitioned between core and shell. From the SANS and interfacial tension data the effective bending constants of the surfactant monolayers were deduced and they show that the extension of the L_α-phase is directly related to a corresponding increase in the bending constants of the surfactant/ester monolayers.

1. Introduction

One of the key properties of surfactants is their capacity to solubilise hydrophobic compounds such as oils, a property, which is for instance of central importance for their application in detergency or pharmaceutical formulations. However, they are also able to incorporate more polar substances such as medium-chain alcohols, aldehydes [1] or ketones [2], carboxylic acids [3,4] or isosorbides [5] which are less considered to be hydrophobic solubilisates but, if polar enough, may function as cosurfactants, i.e. compounds that are surface active but do not form micellar aggregates by themselves. Such more polar compounds are typically not just located in the interior of micellar aggregates but also in the palisade layer [6–8] and therefore modify the state of aggregation by shifting the packing parameter p (given as $p = v/(a_h \cdot l)$, where v, a_h, and l are volume, head group area and length of the amphiphile, respectively [9]), for instance by inducing the formation of long rod-like micelles [10], lamellar phases [11–13] or vesicles [14–20]. Esters with chains of medium length are positioned somewhere between these extremes with respect to their polarity. They are also more flexible with respect to tuning their amphiphilic properties as the alkyl chains of acid and alcohol part can be varied separately. Accordingly their phase behaviour can be more complex as they may possess at the same time the properties of a cosurfactant and of a solubilisate. In addition, the balance between these two characters may depend strongly on temperature and concentration, and, of course, on their detailed molecular architecture.

Typically the solubilisation capacity of aqueous surfactant solutions for oils is rather low and for most surfactants limited to a fraction of an oil molecule per surfactant molecule [21]. This applies in particular to ionic surfactants where the solubilisation capacity normally has to be raised by the addition of a cosurfactant in order to form microemulsions [7,22–24]. In contrast, for nonionic surfactants often one observes much larger solubilisation capacities that can be tuned by changing the temperature [25–27].

One class of nonionic surfactants with a mesoionic character are alkylamine oxides, which show a behaviour between those of typical nonionic and cationic surfactants of identical chain length [28,29]. They have been studied intensively with respect to their solubilisation properties. Hoffmann et al. did show that macroscopic properties such as the solubilisation capacity and microscopic properties such as the head group area are determined by one single parameter: the interfacial tension. From this value it is

---

* Corresponding author. Fax: +49 30 314 26602.
E-mail address: michael.gradzielski@tu-berlin.de (M. Gradzielski).

0021-9797/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2011.06.082

also possible to predict the type of micelles that are formed in surfactant solutions. [22,30]. The solubilisation of hydrocarbons leads to a rod-to-sphere transition, that occurs at the higher oil concentration the shorter the chain length of the hydrocarbon [30]. For the case of hydrocarbon solubilisation it is interesting to note that also the formation of isotropic microemulsion gels of cubic structure can be induced, which contain a molar ratio of surfactant/oil of 2–6, depending on the chain length of the oil and decreasing with shorter oil chain length [31–33]. In contrast, the solubilisation of medium chain alcohols leads first to an elongation of the rodlike micelles and then to the formation of lamellar phases, either in the form of multi-lamellar vesicles (at lower alcohol content) or planar lamellae [34]. Just before reaching the solubilisation capacity then an L_3-phase is observed [35]. In addition, for alkylamine oxides one observes a large increase of the solubilisation capacity for conventional oils upon addition of cosurfactants but already without they can incorporate some amounts of oils [7]. This property renders them interesting surfactants not only for practical applications in detergency [36,37] but also for a systematic study of the effect of the polarity of the solubilisate on its solubilisation properties.

Previous investigations on the zwitterionic surfactant tetradecyldimethylamine oxide (TDMAO) with respect to the solubilisation of the ester methyl heptanoate (enanthic methyl ester, EME) have shown that it can solubilise rather large amounts of that ester and form a low-viscous microemulsion phase at high content (molar ratio ester/surfactant $\approx$ 2:1) of EME. However, at lower ester content (for a molar ratio of about 1:1 of EME/TDMAO) a lamellar phase of multilamellar vesicles is formed, which is relative sensitive to changes in temperature and vanishes for temperatures below 20 °C [38,39]; then a microemulsion is formed. Apparently this ester shows a phase behaviour in between that observed for alcohols and hydrocarbons. Very similar observations have been reported for the addition of hexylacetate or hexylmethylketone, which first behave like cosurfactants and then like hydrocarbons [40]. That interesting behaviour will be generalised in this study with respect to the behaviour of various esters that differ in the chain length of the acid and with respect to its relation to the bending elasticity of the amphiphilic interface.

In our study we concentrated on the effect of the polarity of the solubilisate on the surfactant system and how the phase behaviour and formed microemulsions are affected by that. For that purpose we employed methyl esters of carboxylic acids of various chain lengths that varied from pentanoic to nonanoic, thereby modifying polarity and amphiphilicity of this added oil in a systematic fashion. For these systems we present the phase behaviour, as well as viscosity and interfacial tension. These investigations were complemented by small-angle neutron scattering (SANS) experiments and we worked always at a surfactant concentration of 200 mM. From the systematic variation of the ester length an insight into the relation between the mesoscopic structure and the type of ester employed should be gained.

2. Experimental

2.1. Materials

Tetradecyldimethylamine oxide (TDMAO) was prepared by oxidation of methanolic solution of N,N-dimethyltetradecylamine (Fluka, technical grade $\geqslant$95%) by 30% aq H_2O_2 (Roth, 30–32% wt% in water) solution. After stirring for 1 week at 30 °C and neutralisation with MnO_2, the resulting solution was passed over a silica gel column (elution with dichloromethane) and stored at −20 °C. The precipitate was recrystallised twice from acetone and freeze-dried [41,42]. The cmc was checked to be in agreement with literature values [28,43,44] by surface tensions measurements (see Fig. S1).

All esters, valerian methyl ester (VME), capronic methyl ester (CME), enanthic methyl ester (EME), and pelargonic methyl ester (PME) were purchased from Fluka in p.a. quality and used without further purification. Some relevant properties of the esters are summarised in Table 1. D_2O of 99.9% isotopic purity was obtained from Euriso-top. Scattering length densities of 6.36×10^{-4} nm^{-2} for D_2O and -0.195×10^{-4} nm^{-2} for TDMAO were employed, respectively. For all samples not prepared with heavy water Millipore water was used.

2.2. Sample preparation

All microemulsion samples contained 200 mM surfactant. The samples were prepared by adding a stock solution of 210 mM of surfactant to the required amount of ester and water was added to achieve the final concentration. After homogenising with a vortex mixer the samples were kept for equilibration in a water bath at 25 °C for 1 week and were visually inspected in regular intervals during that time.

2.3. Methods

Electric conductivity was measured with a 712 Conductometer from Metrohm operating at a constant frequency of 300 Hz or 2.4 kHz, which was chosen automatically. A separate double Pt-sheet electrode (Metrohm, 0.15 × 8 × 8 mm) was employed.

For the determination of the zero shear viscosity an Ubbelohde viscometer and micro Ubbelohde viscometer were used. The flow time was automatically determined with a mgw-lauda viscoboy 2 and the average out of three measurements was corrected according to Hagenbach depending on the type of the capillary.

Rheological measurements were performed with a Gemini 200 HR rheometer from Malvern Instruments GmbH. The measurements were carried out with plate–plate geometry (d = 40 mm) and a gap size of 0.15 mm was used. To determine the linear viscoelastic regime an amplitude sweep was performed and from that a deformation of 0.04 for the sample with EME and 0.01 for the one with PME was taken to perform the frequency sweep in controlled strain mode.

Interfacial tensions were determined from spinning drop measurements using a spinning drop tensiometer SITE (Krüss, Germany). The spinning drop tensiometer is based on the theory derived by Vonnegut [46]. A glass capillary was filled with the pure surfactant solution, placed horizontally and equilibrated at 25 °C for 10 min under rotation at ~1000 rpm. One drop ($V \approx 6$ μl) of the less dense ester was placed in the middle of the capillary via a syringe. The rotational speed was increased to 2000–4000 rpm until macroscopic droplets of cylindrical shape were observed in the middle of the capillary. After an initial waiting time of 10 min the diameter of the droplet was measured every 10 min for five times to ensure stable values over one hour. The interfacial tension was calculated according to the following approximation:

$$\gamma = a \cdot d^3 \cdot \omega^2 \cdot \Delta\rho \tag{1}$$

from the average value of the diameter d (determined by the balance between interfacial ($\sim\gamma/d$) and centrifugal ($\sim\Delta\rho \cdot \omega^2 \cdot d^2$)

Table 1
Solubility in water [45], density and scattering length density (SLD) of employed esters at 25 °C.

Ester	Molar mass (g mol^{-1})	Solubility in water (mg l^{-1})	Density (g cm^{-3})	*SLD* (10^{-4} nm^{-2})
VME	116.16	5060	0.88507	0.303
CME	130.18	1330	0.87970	0.235
EME	144.21	309	0.87569	0.181
PME	172.26	23	0.87017	0.107