



The solubilisation of a water insoluble functionalized silicone oil in an aqueous surfactant solution: A novel mechanism for the solubilisation process

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ARTICLE INFO

Article history:

Received 18 May 2010

Accepted 9 July 2010

Available online 13 July 2010

Keywords:

Macromolecular surfactants

Silicone oil

Mixed micelles

Hydrophilic–lipophilic balance HLB

Amphiphile

Solubilisation

ABSTRACT

The solubilisation of the functionalized silicone oil aminoethyl aminopropyl methylpolysiloxane WR 1300 has been investigated in aqueous solutions of the surfactant pentaethoxy-iso-tridecanol ($iC_{13}E_5$). The silicone oil consists of a linear backbone with an average of 200 dimethylsiloxane units and 2–3 functionalized side groups. In various applications the compound is considered a silicone oil. The surfactant $iC_{13}E_5$ forms a L_{α} -phase in water, and with decane a microemulsion can be obtained. The solubilisation experiments started with lamellar $iC_{13}E_5$ phases. With proper amounts of WR 1300 transparent, optically isotropic but highly viscous single phases are formed. These phases cannot be considered true microemulsions with an oil core and a surrounding surfactant layer. Cryo-TEM micrographs show micelles with irregular shapes and about 25 nm diameter. Their size is independent of the oil/surfactant ratio. It can be explained on the basis of a model where the amino groups of the oil are all found at the surface of the micelles, limiting the radius of the aggregates to the largest length of the polydimethylsiloxane backbone between two such groups or between one end of the oil and one functionalized group.

The micellar structures contain only a few siloxane molecules exposing their hydrophilic groups to the water. The functionalized silicone oil molecules can thus be considered as surfactant molecules with a few polar groups and a large hydrophobic chain from dimethyl siloxane.

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1. Introduction

Polydimethylsiloxanes (PDMS) are a class of compounds with remarkable properties. At room temperature they are liquids even when their molecular weights are rather high. Like paraffins, PDMS are not soluble in water and for this reason both compounds are usually called oils. Even the smallest member of the PDMS family, the compound hexamethyldisiloxane, is a volatile liquid that is already insoluble in water. But in spite of their common hydrophobicity PDMS and paraffins are not completely miscible with each other [1]. The low melting points of the PDMS are a consequence of the high flexibility of their backbones [2]. This flexibility is also believed to be the reason for the soft feeling of textiles when they are treated with silicone oils or with functionalized silicone oils [3]. The hydrophobicity and the flexibility of the compounds play a major role in many applications of the pure PDMS compounds and of functionalized PDMS compounds [4]. Because of the hydro-

phobic nature of the siloxane group silicone surfactants are highly surface active compounds [5]. The trisiloxane group is already so hydrophobic that ethoxylated surfactants with this group have a critical micelle concentration as low as 10^{-2} M [5]. In spite of their completely different structures, siloxane surfactants can form the same micelles and liquid crystalline phases as hydrocarbon surfactants [6]. Both globular and rodlike micelles and vesicles are formed from trisiloxane surfactants or silicone surfactants as they usually are called. Micellar solutions of such surfactants have lower surface tensions than hydrocarbon surfactants. A good summary of the synthesis and the properties of silicone surfactants and of PDMS is given in [7].

PDMS compounds with few polar groups are insoluble in water. These functionalized compounds are sometimes also called hybrid PDMS or simply silicone oils. Because of their amphiphilic nature these compounds can be used for the preparation of emulsions [8]. With suitable functional groups that bind to textile fibres the compounds can also be used as textile softener [9]. Because of their insolubility in water, the compounds are usually formulated with non-ionic surfactants to give aqueous solutions. In this manuscript we will report on the solubilisation and the solubilisation mechanism of these compounds in aqueous surfactant solutions.

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Low molecular weight oils can be solubilised into micellar surfactant phases. In the solubilisation process the oil molecules are usually transferred from an oil phase or an emulsion into the interior of micellar structures [10]. In some situations the rate of the solubilisation can be controlled by the solubility of the oil in water. The whole solubilisation process can therefore take a rather long time to reach saturation. When surfactant phases with globular micelles are used for the solubilisation one obtains small o/w droplets which usually contain only few oil molecules. The micelles grow therefore only little in size. With surfactant phases with wormlike micelles the solubility of the oil is higher. Molecules are also first solubilised into the interior of the micelles without a change of the wormlike micelles to occur [11]. Investigations have shown that wormlike micelles can solubilize one or more oil molecules per surfactant and still exist in the wormlike state.

When the oil molecules are larger than the surfactant molecules saturation is usually reached in the wormlike state [12]. Excess emulsion droplets can therefore exist in equilibrium with viscoelastic surfactant system with wormlike micelles. With small oil molecules more oil can be solubilised and the wormlike micelles undergo then a structural change. The micelles change from the wormlike state to the globular state with increasing solubilisation. The transformation occurs within a small oil/surfactant ratio. On further solubilisation the globular o/w droplets can then grow in size and finally reach saturation. With surfactant phases with vesicles the situation is similar [13]. The vesicles first solubilize oil molecules inside the interior of the bilayers of the vesicles. Systems are known in which the vesicles can solubilize several oil molecules per surfactant and still remain in the vesicular state. The vesicles can finally be transformed into o/w droplets or into bi-continuous phases when the solubility is high enough. This is usually the case with surfactant phases that can form microemulsions [14].

In each described situation the solubility of oil decreases exponentially with the size of the oil molecules.

In comparison to fluid hydrocarbon oils functionalized silicon oil molecules are rather large and it is known that linear PDMS molecules with more than five siloxane groups are difficult to solubilize [15]. Large PDMS molecules with more than 10 siloxane groups per one polar group can be solubilised however in surfactant phases, yielding what looks to be microemulsions at first [16]. It is therefore interesting how these molecules are solubilised in surfactant phases and what is the mechanism of solubilisation of these molecules.

The commercially available compound WR 1300 was used for this investigation. It is a PDMS molecule with about 200 dimethylsiloxane units and 2–3 aminoethyl aminopropyl groups. Enough acetic acid was added to provide one proton for each side group, i.e. a total protonation degree of 50%. The compound is mainly used as a softener in textile industry [17]. The compound is not soluble in water, not even in the protonated form. The surfactant pentaethoxy-iso-tridecanol ($iC_{13}E_5$) was used for the solubilisation experiments. This surfactant forms a lamellar phase in aqueous solutions and it is known that surfactant solutions which form lamellar phases have low interfacial tensions against oil phases [10]. It could therefore be hoped that the solubility of WR 1300 in the surfactant phases is high. One of the goals of the investigations actually was to find out whether the WR 1300 can form a microemulsion with $iC_{13}E_5$.

The solubility of oil molecules in surfactant solutions or in microemulsions decreases exponentially with the molar volume of the oil molecules [18]. The reason for this situation is that the energy $\sigma \cdot v$ has to be overcome in the solubilisation process in which σ is the interfacial tension of oil against water and v is the molar volume of the oil. The solubility of an oil can therefore be optimized by using a surfactant solution that has a low interfacial

tension against the oil. Surfactants that give low interfacial tensions against an oil phase are surfactants that produce liquid crystalline L_α -phases at low concentration [10]. But even for optimized conditions oils with large molecular weight are not soluble very much. This is the reason why microemulsions were always prepared from low molecular weight paraffin or from low molecular weight esters [19].

In the present work, we have investigated the solubilisation of a large silicone oil molecule with very few polar groups in a surfactant solution.

2. Materials and methods

2.1. Cryogenic transmission electron microscopy cryo-TEM

For the cryo-TEM studies, a drop of the sample was placed on a lacey carbon copper transmission electron microscopy (TEM) grid (200 mesh, Science Services, Munich, Germany) which was hydrophilized by glow discharge prior to usage. The majority of the liquid was removed with blotting paper, leaving a thin film stretched over the grid holes. The specimens were then shock-vitrified by rapid immersion into liquid ethane and cooled to ca. 90 K by liquid nitrogen in a temperature-controlled freezing unit (Zeiss Cryobox, Zeiss NTS GmbH, Oberkochen, Germany) [20]. The temperature was monitored and kept constant in the chamber during all of the sample preparation steps. After the specimens were frozen, the remaining ethane was removed using blotting paper. The specimen was inserted into a cryo-transfer holder (CT3500, Gatan, Munich, Germany) and transferred to a Zeiss EM922 Omega EFTEM instrument. Examinations were carried out at temperatures around 90 K. The transmission electron microscope was operated at an acceleration voltage of 200 kV. Zero-loss filtered images ($\Delta E = 0$ eV) were taken under reduced dose conditions (100–1000 e/nm^2). All images were registered digitally by a bottom-mounted slowscan CCD camera system (Ultrascan 1000, Gatan, Germany) combined and processed with a digital imaging processing system (DigitalMicrograph, Gatan, Munich, Germany).

The viscosity was measured on a ThermoHaake RS 600, equipped with a thermo-controller TC81, using a cone-plate geometry with a 60 mm diameter, 1° angle titanium cone.

The WR 1300 is a product of the Wacker Chemie AG, Burghausen. The $iC_{13}E_3$, $iC_{13}E_5$ and $iC_{13}E_8$ are products of the Sasol AG, Hamburg, Germany.

3. Experimental results and their discussions

3.1. The phase diagram of $iC_{13}E_5$

The compound $iC_{13}E_5$ is commercially available as a waterless compound. It has a density of ca 1 g cm^{-3} and it can easily be dispersed in water. Samples with increasing concentration of $iC_{13}E_5$ up to 20% are shown in Fig. 1 in which the upper row of the samples were photographed with normal illumination while the lower row of samples were photographed between crossed polarizers.

As judged from the upper row the samples with up to 10% of $iC_{13}E_5$ are not completely clear but seem to be homogenous. The turbidity is the same in the whole sample. The birefringence in the samples between the polarizers indicates however that these samples are not completely homogenous. The samples show a stronger birefringence on the top of the samples than on the bottom. This is a sign that these samples are in a two phase situation; they are already demixed on a microscopic level and are on the way of macroscopic demixing. However due to the small density differences the demixing takes a long time. No sharp phase boundary has developed in the phases. The samples with more than 10%

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