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Recent developments in the characterisation of microemulsions

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Abstract

Microemulsions are becoming increasingly complex systems by containing more sophisticated surfactants, polymers, biomolecules, inorganic nanoparticles, etc. The detailed understanding of such more complex systems requires increasingly more refined and comprehensive characterisation. This is typically done by the combination of complementary techniques and is aided by the fact that several experimental methods have been improved (such as electron microscopy) in recent times, new ones have become available (such as fluorescence correlation spectroscopy), and the theoretical understanding of structural data is advancing.

Keywords: Microemulsions; Solubilisation; Surfactants; Characterisation techniques

1. Introduction

Microemulsions are self-aggregated systems in which oil and water are homogenously mixed due to the presence of amphiphiles. They are isotropic with typical structural units in the size range of 3–30 nm from which their transparent appearance results. They differ from conventional emulsions not only by their much smaller structural size but in particular by their thermodynamic stability, which renders them very interesting systems as they allow for a long-lived stabilization of mixed oil/water systems, which otherwise can not be achieved.

Microemulsions have been the topic of comprehensive research for more than 40 years with a particularly intense period in the late 70s and early 80s in the context of tertiary oil recovery [1]. Due to substantial improvements of experimental characterisation techniques in that time, most prominently electron microscopy [2], scattering techniques like dynamic light scattering (DLS), small-angle X-ray scattering (SAXS), and, in particular, small-angle neutron scattering (SANS) [3], nuclear magnetic resonance (NMR) [4,5], as well as various other techniques [6] a good knowledge of the structure of microemulsions was obtained. As at the same time important developments in the theoretical description were advanced [7–9] a rather comprehensive picture of the properties and behaviour of microemulsions was obtained. It should be noted that especially the combination of various experimental techniques (e.g. direct imaging and scattering methods) [6] and its connection with appropriate theoretical models is required in order to deduce a more refined structural picture. That aspect has become increasingly important in recent years, where the systems studied have become increasingly more complex in terms of their composition, e.g. containing polymers, biomolecules, complexing surfactants [10], nanoparticles and/or mixtures of surfactants. So the main direction of current developments in the characterization of microemulsion systems is to address their increasing structural complexity in composition.

However, due to this potential complexity of composition more comprehensive studies on microemulsions are required, as, depending in particular on the nature of the amphiphile, the detailed properties of microemulsions may vary largely. In the following we want to give a brief description of recent developments in the characterisation of microemulsions which is mainly concentrating on developments in the field of characterization methods, but partly also reflects their increasing complexity with respect to contained constituents. Accordingly, this article is subdivided into paragraphs dealing with certain experimental techniques and also according to their composition

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(e.g. containing polymers). However, it should be noted that due to challenge of the complexity of the structures contained typically various experimental techniques have to be combined (at best also with corresponding theoretical models) and our assignment is therefore somewhat arbitrary and reflecting our subjective view of what is the most important aspect in a given research work.

2. Electron microscopy

Very significant advances have been achieved in recent years in the field of electron microscopy and, in particular, with respect to the technique of cryo-transmission electron microscopy [10]. For instance, this concerns the much enhanced sensitivity that allows to work at very low dose which enables one to study very delicate cryo-fixed samples. With corresponding sophisticated equipment with doses less than 100 electrons/nm^2 still detailed electronmicrographs can be obtained. This is a very important point for such sensitive structures as microemulsions, as otherwise the samples are damaged easily either by simply heating them or breaking of covalent bonds.

In addition, procedures have been established that allow to prepare and image delicate samples in a reliable way, thereby minimizing the effect of artefacts. Another aspect is related to the development of novel techniques, that allow to prepare cryo-fixed samples under less invasive and more reproducible conditions. This is a very important aspect as microemulsions (as amphiphilic systems in general) are often very sensitive to the rather vigorous conditions of cryo-fixation that involve high shear rates, the risk of evaporation, or the rearrangement of the structural entities during the preparation process due to the fact that the cryo-fixed samples contain a very high surface to volume ratio.

The increased sensitivity not only allows for a much more effective observation of samples but in a novel technique called "freeze–fracture direct imaging" it is also usefully employed in the direct observation of samples that are obtained by the freeze–fracture method and are observed directly, i.e. without having to form a replica first. The advantage is that here one avoids the blotting procedure where the high shear rates can influence the formed structures and, in addition, one pictures the situation in the bulk phase, which is not necessarily the case for cryo-TEM. A direct comparison between the results of this technique and conventional cryo-TEM enhances the reliability of the observed structures largely and thereby minimizes the risks of artefacts. The applicability of this method was demonstrated for the case of W/O and bicontinuous microemulsions, both of which are very difficult or not at all to be prepared by cryo-TEM [11•].

Nonetheless cryo-TEM is a powerful tool that was successfully employed to characterise the structure of O/W microemulsions formed by didodecyldiphenylether disulfonate gemini surfactants (or its corresponding single chain alternatives) with toluene as oil and in the presence of 1-propanol, 1-butanol, or 1-pentanol as a cosolvent. Both O/W and W/O microemulsions are formed which contain globular as well as strongly elongated aggregates. This is interesting as it demonstrates that the already existing tendency of gemini surfactants to form elongated rod-like micelles also persists for the case of microemulsions [12].

3. Scattering techniques

Scattering techniques such as static and dynamic light scattering (SLS, DLS) and, in particular, small-angle neutron and X-ray scattering (SANS, SAXS) have been instrumental in the original structural characterisation of microemulsions [3,13], and they are still widely employed in order to determine the structural features of microemulsions with an Å resolution, in order to obtain a detailed picture of the build-up of the microemulsion structure.

Knowledge of the bending moduli of the amphiphilic monolayers remains a key quantity for the understanding of microemulsions. The description of the amphiphilic mono- or bilayers has originally been proposed by Helfrich according to which the free bending energy F_b is given by [14]:

$$F_b = \int \left\{ \kappa/2 \cdot (c_1 + c_2 - 2 \cdot c_0)^2 + \overline{\kappa} \cdot c_1 \cdot c_2 \right\} \cdot dA$$

where c_1 and c_2 are the principal curvatures of the surfactant film, c_0 its spontaneous curvature, and κ and $\overline{\kappa}$, the mean and the Gaussian (or saddle–splay) modulus, respectively.

A very direct way to determine the mean bending modulus κ is classically given by the neutron spin–echo (NSE) method which allows to measure the shape fluctuations of droplets and, in combination with SANS experiments, to deduce directly κ and $\overline{\kappa}$, in an independent fashion [15]. A recent application of this technique to W/O microemulsions based on sodium bis(2-ethylhexyl) sulfosuccinate (AOT) in cyclohexane, hexane or compressed propane yielded rather low values of 0.2–0.3 kT for the mean bending modulus κ of the surfactant monolayer [16]—which is in striking difference to former values derived for AOT/decane/water W/O microemulsion droplets derived by a similar approach [17]. The addition of octanol as a cosurfactant to these microemulsions was shown to have only a minor effect on κ, a result that was similarly observed before for the case of O/W microemulsions for such medium-chain alcohols [18]. In a similar way classical nonionic O/W microemulsions with pentaethyleneglycol monododecyl ether ($C_{12}E_5$) with decane or hexadecane as oil have been reexamined in terms of their bending moduli. The combination of phase studies with SAXS and ^{2}H-NMR relaxation experiments allowed to deduce a detailed structural picture that was interpreted in such a way that an increase of the chain length of the oil leads to a moderate increase of the Gaussian modulus $\overline{\kappa}$, while the mean bending modulus κ remains unaffected [19].

In a very interesting study the effect of the architecture of the hydrophobic part of nonionic microemulsions on the structure and properties of the formed microemulsions was studied. For that purpose $C_{10}E_5$ surfactants with various linear and branched decyl chains were synthesized and their phase behaviour with respect to forming bicontinuous microemulsions