Consistent definitions of "the interface" in surfactant-free micellar aggregates

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HIGHLIGHTS

- Surfactant-free micelle aggregates are studied with molecular dynamics simulations.
- Aggregates of the different preferred aggregation numbers are analyzed.
- Different criteria for an interface definition are tested.
- The location of the interface can be defined in a consistent way.

GRAPHICAL ABSTRACT
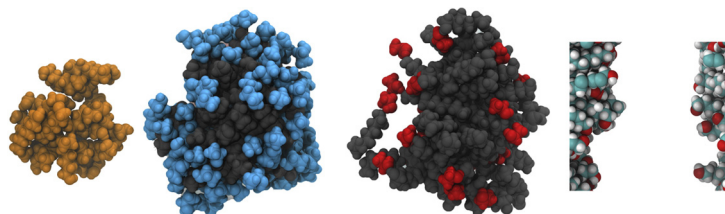
Consistent Definition of Interface

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ABSTRACT

The theoretical description of systems with soft interfaces requires a precise definition of the interfaces that are present. Such definitions are common for interfaces of simple liquids and for surfactant assemblies like micelles, membranes, and microemulsions. Here, we focus on several possible rigorous definitions in a recently described surfactant-free microemulsion that consists of octanol, ethanol, and water, in which micelle-like aggregates are in dynamic equilibrium with the surrounding pseudo phase. We test different definitions that are based on the radial distribution functions of the components with respect to the center of these surfactant-free micelles. All definitions result in experimentally indistinguishable locations of the interface within the limits of resolution of light, X-ray, and neutron scattering experiments, since their locations differ by at most 0.4 nm, which corresponds to roughly 2-3 bond lengths.

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1. Introduction

The thermodynamic discussion of systems with two phases or pseudo-phases involves the definition of the interface as one of the essential steps [1]. Based on this definition, the excess properties of this interface and their thermodynamic consequences can be analyzed [2]. The exact definition of the interface is however subject to some ambiguity and it depends on the type of system, which definitions are possible and meaningful.

At a vapor/liquid interface, the common definition of the interfacial plane is the Gibbs dividing surface (GDS), which is the plane for which the liquid has zero interfacial excess. Other definitions like the plane of maximum density gradient (inflection point of the density profile) or the point at which the density is half of the bulk value usually coincide with the location of the GDS at vapor/liquid interfaces, which have a symmetrically shaped density profile.

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These definitions are extendable to liquid/liquid interfaces, in which case the density can be split into the partial densities of the two phases [3]. In this case, a typical definition for the interface is the plane at which the two densities – normalized to their bulk values – are equal [4]. This however can lead to an inconsistent interface location, because a definition using the density profiles can lead to a different position than a definition based on the position of the neutral plane of bending [5]. Moreover, for these interfaces the density profiles are not necessarily symmetric and even different density-based definitions of the interface need not to coincide. This is problematic, because for the prediction of phase diagrams a lateral equation of state is needed, which requires an operative definition of the interface [6]. The consistency of the interface location becomes especially crucial for interdigitated or weakly associated surface layers such as those formed by carboranes, since water molecules are present on *both* sides of the interface [7].

When interfaces of solutions are studied, the Gibbs dividing surface is especially useful for the determination of surface tension increments [8]. When surfactants are present at the interface, their preferred position is naturally close to the interface in any of the senses mentioned so far. Therefore, the surfactants themselves can be employed for determining the interface. For charged surfactants, e.g., a plane of fixed charge has been employed. [9]

In the special case of surfactant solutions, micellar systems, the nature of the interface depends strongly on the type of micelle under consideration. Precise definitions of the location of the "interface" have been proposed for ionic [10] and nonionic micelles [11] as well as for oil soluble surfactants [12], allowing for precise evaluations of the free energy per unit surface as a function of the area per molecule.

Recently, scattering experiments with light, X-rays, and neutrons [13–15] demonstrated the existence of micelle-like aggregates of 20–100 molecules in thermodynamically stable ternary solutions, in which an ethanol-soluble but water-insoluble compound like octanol is dissolved in an ethanol/water mixture. Micelle-like aggregates form in these systems even if these systems do not match the classical picture of self-aggregating surfactant molecules. It was argued that in these systems the ethanol molecules play the role of a hydrotrope that mediates the solubility of the 'nonpolar component'. Classical force-field molecular dynamics simulations were applied for a detailed molecular analysis of these systems [16]. These simulations showed an aggregate size distribution that is distinctly different to simple aggregation in binary solutions [17] or to percolation of water in a binary solution [18].

In this work we closer analyze the structure of the differently sized preferred aggregates that were observed in simulations and compare this to the properties of a flat water/octanol interface in the presence of a small amount of ethanol. We derive and compare different definitions for the interface between the two pseudo-phases and discuss their implications.

2. Results and discussion

The simulations of a macroscopically stable one-phase system comprising octanol ($N_{Oct} = 224$), ethanol ($N_{Eth} = 6366$), and water ($N_{Wat} = 21\,839$) reveal that the histogram of aggregate sizes shows several broad peaks. These peaks correspond to preferred aggregates that occur for octanol aggregation numbers N approx. equal 22, 33, 55, and 100. In Fig. 1, we show exemplary aggregates with these aggregation numbers. We demonstrate the generality of the interface definition by showing the results of a planar water/octanol interface in the presence of ethanol with a concentration similar to the aggregate systems. The aggregates of size 22, 33, and 55 are
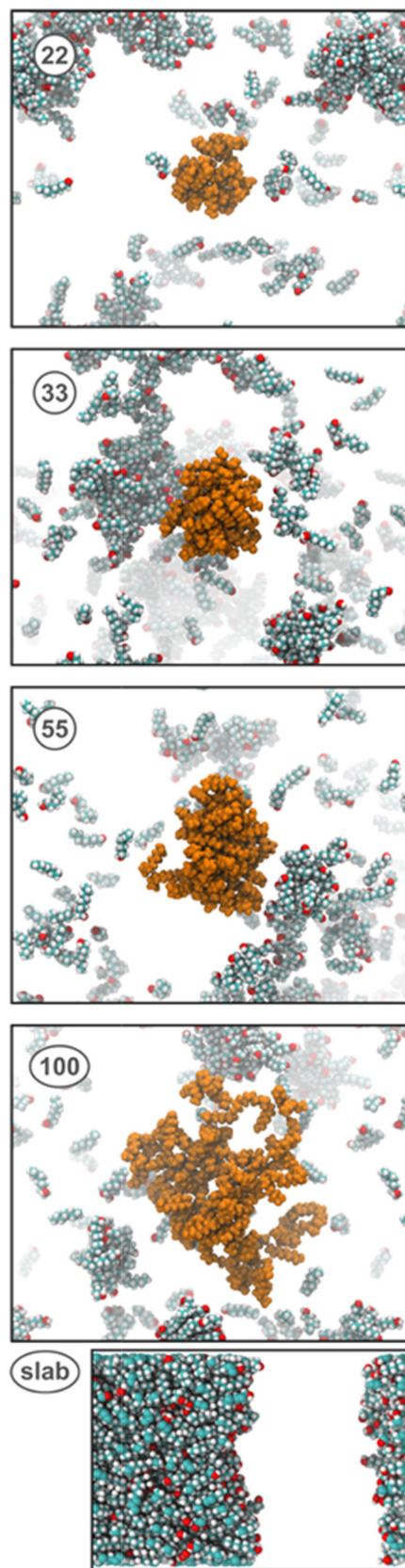

Fig. 1. Snapshots of the different aggregates of size 22, 33, 55, and 100, and of the planar interface with 5% ethanol in the aqueous phase. Shown are only the octanol molecules. The three smaller aggregates clearly correspond to one concise object. To the contrary, the aggregate with 100 octanol molecules comprises more than one object that are grouped together as an artifact of the algorithm used for aggregate determination.