



# Depletion of water-in-oil aggregates from poor solvents: Transition from weak aggregates towards reverse micelles



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## ABSTRACT

We assemble here all available descriptions of oil-soluble surfactant aggregates with or without solutes, assumed to be located in the polar cores of reverse micelles. The presence of solutes is crucial for the formation of a well-defined interface, thus inducing a transition from a loose reverse aggregate into a more structured micelle. This transition can be followed by the concomitant decrease of the “critical aggregation concentration” (*c.a.c.*). The less organized state as reverse aggregates is predominant when no “nucleating” species such as water, salts, or acids are present. One way to understand this weak aggregation is a depletion driving to aggregates as pseudo-phases introduced by Tanford. Analogues coexisting pseudo-phases seem to exist: weak oil-in-water (o/w) aggregation with the so-called surfactant-free microemulsions, containing loose aggregates, and re-entrant phase diagrams presenting a lowest aggregation concentration (*l.a.c.*), as described in the seventies.

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## 1. Introduction

“Extractants” are a class of oil soluble multi-chain surfactants with ultra-low solubility in water, some solubility in solvents and a tendency to form viscous solutions or strong gels in the presence of a third component, such as water. “Reverse micelles” is the term used when each water-in-oil (w/o) micellar aggregate contains enough solutes (water or salts) to form a well-defined fluid “polar core”. As can be seen by high resolution X-ray or neutron scattering [1,2], this polar core separated from the solvent by a highly curved extractant film belongs to the class of microemulsions. A well-defined liquid core is detectable by NMR or by high precision density measurements [3] as soon as the number of water molecules per surfactant exceeds the number of molecules in the first hydration layer of the surfactant head-groups [4].

“Is water necessary to the formation of micelles in apolar media?” [5]. This very important question was addressed thirty-five years ago. The answer can be “yes” and “no”:

- “Yes”, because in all examples for which ternary phase diagram as well as microstructure has been determined via combined SANS/SAXS on a wide  $q$ -range, more than one “solute” molecule – such as water or acetonitrile – is required to form a reverse micelle with a well identified polar core [6]. The most direct experimental proof

of the existence of a well defined interface separating two immiscible liquids is the presence in any scattering experiment of a well defined “Porod-type” power-law decay [7,8]. The value of the area per molecule immediately gives the area per surfactant molecule present [9] and the amount of monomers coexisting in dynamic equilibrium is experimentally difficult to determine and is roughly in the order of  $10^{-3}$  M for all cases described up to now [10].

- “No” because there are recent experimental reports by Rodrigues [11] and Ferru [12] about well determined w/o aggregates, with four to height molecules per aggregate, that do not show a measurable Porod limit decay in scattering. These aggregates are in dynamic equilibrium with monomers of extractant dispersed in the solvent.

These weak aggregates are structurally less constrained than classical reverse micelles, i.e. polar weakly bound cores dispersed in apolar medium as loose aggregates coexist with large amount of extractants in monomeric form (typically 0.1 M). On the contrary, classical structured reverse micelles are aggregates with a well-defined polar core volume: a Porod-type  $q^{-4}$  decay in scattering is observed and each aggregate contains 30 to 3000 surfactant, with a water to surfactant molar ratio between 6 and 300, as reported up to now.

The area per molecule adopted is the value which minimizes the free energy [13]. The volume of core per extractant molecule is the sum of the volumes of polar liquid in the core. For the most studied reverse micelle made with the extractant AOT, the area per molecule

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is  $0.6 \text{ nm}^2/\text{molecule}$  in all solvents. This is the reason why the curvature radius of the polar liquid balances with  $[\text{AOT}]/[\text{water}]$  mole ratio [1]. For weaker aggregates with less than four water molecules per extractant, the geometrical constraints are not dominating the microstructure [14]. The aggregation number, i.e. the number of molecules per aggregate is driven towards lower number of molecules per aggregates by the mixing entropy [15] while electrostatics [16] and dispersion forces [17] favour larger aggregates. Packing effect can influence smaller or larger aggregation numbers [18]: aggregation numbers have been reported mainly in the range of 10 to 1000 hydrophobic chains per reverse micelle [14] and in the range of 4 to 20 for weak w/o aggregates [19].

“Micelles” are classically distinguished from progressive aggregation such as dyes in water: when a preferred number of aggregation exists [20], the concept of micelles is used while progressive aggregation or fluctuation only is characterised by a monotonic decrease of the concentration of aggregate with the aggregation number [21]. Progressive aggregation is common in water for pigments, aroma and inorganic species. Progressive aggregation with no preferred aggregation number must be distinguished from micelle formation by the existence in the latter of a well defined maximum of the free energy of formation versus the average number of molecules per aggregate, or equivalently the area per molecule [22]. Since monomers are always in dynamic coexistence with reverse aggregates, an equivalent way to rationalize these extrema in the free energy function is the existence of a minima in the distribution function between the monomer ( $N_a = 1$ ) and the micelles [23]. If the number of molecules per aggregate is lower than half a dozen, it may be useful to describe the thermodynamics of self-assembly within the multiple equilibrium model. Within the frame of the pseudo-phase model [24], the “monomers in solvent” pseudo-phase is considered in dynamic exchange with one “reverse micellar” pseudo-phase containing all molecules present in the aggregates. There is a macroscopic separation between pseudo-phases. Since this approach reduces the number of parameters in the description of solvent rich organized fluids, it may be more useful, due to the limited number of parameters needed, to predict behaviours such as ion activity or solvent activity which are related to vapour pressures, following the line by Charles Tanford [24]. The two models are equivalent for aggregation numbers with fewer chains per reverse aggregate, as shown in Fig. 1. Within both equivalent approaches, the critical micellar concentration is a well defined concept and is related to the free energy of transfer of a given surfactant/extractant from the solvent pseudo-phase to the micellar pseudo-phase [6]. It is important to notice that micelles exist at total concentration of solubilized surfactants lower critical micelle concentration (*c.m.c.*) when aggregation number is not infinite [25]. Moreover, the concentration of monomers is constant and similar to the *c.m.c.* in value at any total concentration beyond the *c.m.c.* These values can be calculated in both pseudo-phase or multiple equilibria models, as shown in Fig. 1.

Experimental efforts were made to thoroughly desiccate solvents and avoiding any intrusion of water while dissolving an “extractant”,

i.e. the surfactant molecule that is soluble in the solvent, but nearly insoluble in water (much less than 1 mM), with consequences on the observed phase behaviour [26].

In this case, the critical micellar concentration was shown to exhibit a re-entrant behaviour. At a very low chemical potential of dissolved water, the *c.m.c.* is of the order of  $30 \mu\text{mol}$  in the presence of  $10^{-6}$  moles of residual water, while is three times less in the presence of  $10^{-3}$  moles of residual water in the solvent. The order of magnitude is a factor of six, i.e. 1 to 2 kT per water molecule, a little less but the same order of magnitude than one hydrogen bond, showing that hydrogen bonds between water molecules in reverse aggregates are crucial in the formation of reverse aggregates free energy (see [5,14] and the references therein). Note that a similar behaviour is observed for micelles made by short chain amphiphiles in water: solutes of larger molar volume than the surfactant become soluble even *below* the *c.m.c.* This general behaviour, where the solute induces the formation of a micelle, has been discovered by Per Ekwall and has been named “*l.a.c.*” for the lowest aggregate concentration. This *l.a.c.* phenomenon is qualitatively understood, but to our best knowledge, no general predictive model is available yet.

## 2. Reverse micelles and reverse aggregates: the role of nucleation

Closer examinations of extractant aggregate formation in pure n-heptane have shown that the amount of water molecules, and/or cation salts has a significant influence on these aggregate shapes [27]. Solvent extraction experiments involve an interfacial transfer of a coordinating metal ion from an aqueous solution into a water-poor microemulsion [25]. The organic phase resulting from this kind of experiments are usually solutions of “hard” metal complexes [28] in “soft” amphiphile-in-oil aggregates, present either as neighbouring aggregates or loose continuous networks [29]. In the case of monoamide and diamide extractants, the combination of small and wide X-ray scattering with molecular dynamic simulations has shown that these aggregates may exist even in the absence of any extracted metal, i.e. in the absence or at low concentrations of polar structuring constituents. A schematic representation as a guide for intuition of these aggregates is shown in Fig. 2. As can be seen on the left part of Fig. 2, the relative positions of the extractant polar heads do not form a 2D curved film, unlike the scheme on the right. The introduction of a cation salt in the same organic solution converts the aggregate structure into classical reverse micelles with a strong polar core enclosed in an aliphatic crown (as shown in Fig. 2, right). The scattering patterns obtained by SANS or SAXS are similar for the two types of aggregates. Moreover, the two forms coexist at low “metal load”, and this coexistence is in our opinion the reason for which these two states of extractant aggregates have not been clearly distinguished so far in the literature in the speciation of the solvent phase used in liquid-liquid extraction processes. Furthermore, classical representation with multiple equilibria does not distinguish between aggregation numbers ( $n_{\text{agg}}$ : the time-averaged numbers of molecules

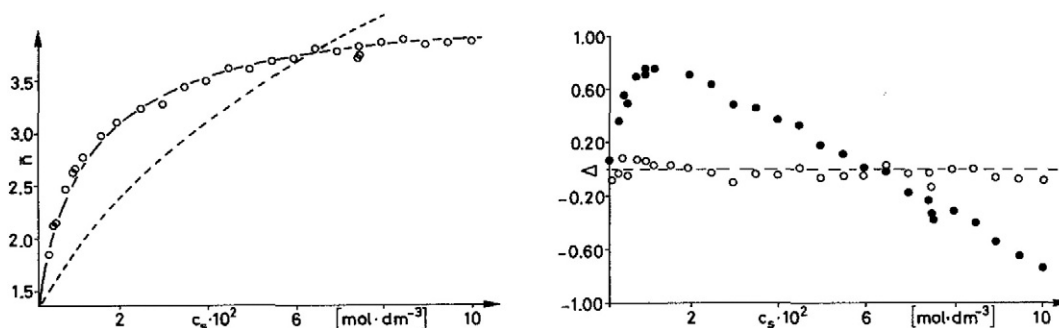


Fig. 1. Left: average aggregation number versus DAF (dodecyl-ammonium-formiate) concentration ( $C_s$ ) in benzene at  $25^\circ\text{C}$  using pseudo-phase (plain line) or equilibrium (dashed line) models. Right: residuals  $\Delta$  of experimental points and theoretical models for the above systems:  $\circ$  from Pseudo-phase model,  $\bullet$  from the multiple equilibrium model [10].

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