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Colloids and Surfaces A: Physicochemical and Engineering Aspects

The effect of solvent and counterion variation on inverse micelle CMCs in hydrocarbon solvents

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HIGHLIGHTS

- CMCs for inverse micelle formation can be measured using neutron scattering.
- CMCs for Aerosol OT in aliphatic and aromatic solvents are essentially the same.
- CMCs for sodium and tetrapropylammonium Aerosol OT are essentially the same.
- Surfactants are too solvophobic for these variations in structure to influence the CMC.

GRAPHICAL ABSTRACT
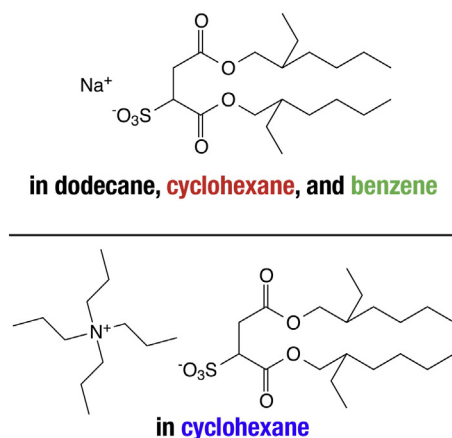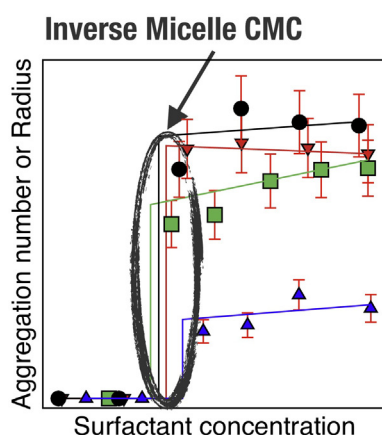
ABSTRACT

Critical micelle concentrations (CMCs) for the formation of inverse micelles have been determined for anionic surfactants in nonpolar, hydrocarbon solvents. Sodium dioctylsulfosuccinate (Aerosol OT or AOT) was chosen as the model surfactant, with systematic variations in both the solvent (benzene, cyclohexane, and dodecane) and the surfactant counterion (sodium and tetrapropylammonium). Recent work (*Langmuir* 29 (2013) 3352–3258) has shown that high-resolution small-angle neutron scattering (SANS) measurements can be used to directly determine the presence or absence of aggregates in solution. No variation in the value of the CMC was found within the resolution of the measurements for changing either solvent or counterion; some effects on the structure of inverse micelles were observed. This lack of a significant difference in the onset of inverse micellization with changes to the molecular species is surprising, and the implications on the solvophobic effect in nonpolar solvents are discussed.

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1. Introduction

Klevens proposed a now well-known relationship between the critical micelle concentration (CMC) of a homologous series of linear chain surfactants in water and the number of carbon atoms in the tails, n_c [1,2].

$$\log(\text{CMC}) = A_K - B_K n_c \qquad (1)$$

A_K depends on the surfactant headgroup (the "hydrophilic" part of the molecule). For ionic hydrocarbons, the value of B_K is empirically $\log 2$, and it scales the effect of the length of the hydrocarbon chain (the "hydrophobic" part) on the value of the CMC. Literature data for CMCs of sodium dialkylsulfosuccinate and alkylsulfate salts with different n_c values in water are shown in Fig. 1. $\log(\text{CMC})$ is indeed proportional to n_c, and the gradient is -0.31 for dialkylsulfosuccinates and is -0.29 for alkylsulfates ($\log 2 \approx 0.30$). Increasing the surfactant chain length decreases the CMC. Tanford has shown that micellization in water occurs due to the hydrophobic effect, and the contribution of adding hydrocarbon groups to the free energy of micellization can be calculated from $RT(\mathrm{d}\ln\text{CMC}/\mathrm{d}n_c)$. The decrement in Gibbs energy of micellization is $\sim 3\,\text{kJ mol}^{-1}$ per CH_2 group, although it is reduced for ionic surfactants in water due to the background ionic strength of the free surfactant [3,4].

Changing from water to a nonpolar solvent (with relative permittivity, $\epsilon_r \approx 2$) significantly influences the nature of the surfactant–solvent interactions; the terms hydrophilic and hydrophobic lose meaning. Rather, the two parts of the molecule are better described as "solvophilic" and "solvophobic." In nonpolar solvents, the alkyl tails are solvophilic (in water, hydrophobic), and the ionic headgroups are solvophobic (in water, hydrophilic). This has the consequence of inverting the aggregate structure; sodium dioctylsulfosuccinate (Aerosol OT or AOT), for example, forms inverse micelles and reverse water-in-oil (w/o) microemulsions [8]. The Klevens equation can still apply in nonpolar solvents, as long as n_c is replaced by the number of solvophobic groups. Fig. 1 shows how the CMC varies with the number of ethylene oxide solvophobic groups for nonionic surfactants in hexadecane [7]. There is still a linear relationship between $\log(\text{CMC})$ and the number of solvophobic groups, but the slope is now different. The nonaqueous solvent B_K per solvophobic group for ethylene glycol dodecyl ethers in hexadecane is 0.10 or $\log 1.2$. Solvophobicity is an additive property in alkane solvents, just like in water, and it is directly related to the surfactant molecular structure. The decrement in Gibbs energy of micellization per solvophobic group is less for ethylene glycol dodecyl ether surfactants in hexadecane than it is for sodium alkylsulfate or dialkylsulfosuccinate surfactants in water. This group contribution is found to be $\sim 0.5\,\text{kJ mol}^{-1}$ per ethylene oxide group in hexadecane, compared to $\sim 3\,\text{kJ mol}^{-1}$ for CH_2 groups in water, despite the larger number of atoms per solvophobic group.

In this paper, derivatives of the model anionic surfactant AOT are studied in nonpolar solvents. This surfactant does not have a solvophobic increment like the surfactants shown in Fig. 1, but AOT is an interesting and well-studied model surfactant that is important in numerous applications as, for example, a microemulsion stabilizer [8], as a micellar nanoreactor [9], or as a charge control agent [10]. Understanding how this surfactant forms inverse micelles at low concentrations is important for efficient and controllable use in applications. Given that there is no solvophobic group to vary in AOT, how would the Klevens equation apply to such a system? The solvophilicity index (A_K) now relates to the hydrocarbon tails, and the solvophobicity parameter (B_K) now relates to the surfactant headgroups. As solvophobicity is driven by the ionic group, $B_K n_c$ now needs to be thought of as a single variable. The equation now takes the form $\log(\text{CMC}) = A_K - B_K$. This two-parameter equation demonstrates the concept that aggregation is a balance between solvophilicity (A_K) and solvophobicity (B_K). The solvophobicity of the AOT cannot be readily changed as it is defined by the molecular structure; on the other hand, the solvophilicity of AOT can be readily changed by varying the solvent quality [11].

The existence of a CMC for inverse micelle formation is still debated [12,13]. (In this paper, the CMC from now on refers to the critical concentration for inverse micelle formation, unless otherwise stated.) Experimentalists, however, have succeeded in measuring transitions that are consistent with a step change from monomers to inverse micelles at a critical concentration [14–22]. Accurate and consistent values of CMCs for inverse micelle formation are lacking in the literature. Several groups have used techniques as disparate as iodine solubilization and mercury interfacial tension to measure CMCs for AOT in different organic solvents, but the results are highly variable between the different studies [15,16,19,20,23,24]. Measuring CMCs in organic solvents is challenging experimentally. Techniques frequently used to detect CMCs in water (conductivity, surface tension, or dye solubilization) have drawbacks that make them ill-suited to detect inverse micelle CMCs in organic solvents [22]. Due to high contrast and sensitivity, small-angle scattering measurements provide perhaps the strongest experimental evidence for a critical micelle concentration in aliphatic and aromatic nonpolar solvents [18,22,25,26].

To compare aggregation of surfactants in nonpolar solvents to water, suitable molecular variations need to be studied, analogous to the $B_K n_c$ term in Eq. (1). For surfactants in water, extending the tail length makes the surfactant more solvophobic. However, changing the surfactant tails is not viable in nonpolar solvents; they are now the solvophilic groups. Instead, changes to the counterion and the solvent are made in this study. The CMC of AOT in three organic solvents (benzene-d_6, cyclohexane-d_{12}, and dodecane-d_{26}) and of an analogue, where the Na^+ counterions have been exchanged for tetrapropylammonium cations (TPA-AOT) in cyclohexane-d_{12}, were measured. Varying the identity of the solvent would be expected to modify the solvent quality for surfactant tails, and changing from a hard counterion (Na^+) to a soft counterion (TPA$^+$) would be expected to modify the surfactant solvophobicity. The effect of varying surfactant structure on the formation of micelles in water is well-known, but the effect of these variations on the formation of inverse micelles in nonpolar solvents cannot be predicted. High-resolution small-angle neutron scattering (SANS) measurements have been
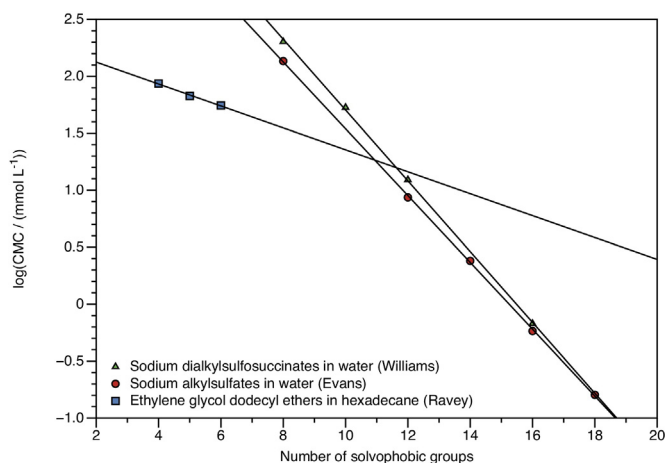

Fig. 1. Klevens equation plots (log(CMC) versus number of solvophobic groups) for three systems of amphiphiles (sodium dialkylsulfosuccinates in water [5], sodium alkylsulfates in water [6], and ethylene glycol dodecyl ethers in hexadecane [7]). For ionic surfactants in water, the trend is known from Klevens's publications [1,2], and it has a gradient of $\sim \log 2$. For the nonionic surfactants in hexadecane, the CMC also depends on the number of solvophobic groups, although the gradient is shallower.