

The selective partitioning of the oligomers of polyethoxylated surfactant mixtures between interface and oil and water bulk phases

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Abstract

Because their affinities for the oil and water phases vary considerably with the number of ethylene oxide units in their hydrophilic group, the ethoxylated nonionic species occurring in commercial products tend to behave in a non-collective way, with the low ethoxylation oligomers partitioning mostly in the oil phase. This results in a surfactant mixture at the interface which is more hydrophilic than the one which was introduced in the system in the first place. The pseudophase model is used to study the partitioning in Winsor III type systems, and to estimate the deviation of the interfacial mixture composition from the overall one. New results indicate that the selective partitioning into the oil phase increases when the oil phase becomes aromatic, when the total surfactant concentration decreases and when the water-to-oil ratio decreases.

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1. Introduction

When two surfactants are present in a surfactant–oil–water (SOW) system, selective partitioning can take place depending on the manner the two amphiphilic species behave. If they behave in

some collective manner, i.e., if the amphiphilic mixture in each phase and at interface has the same composition as the overall mixture, then it behaves as a single amphiphilic component and is sometimes referred to as a pseudocomponent. Although this is an easy-to-handle situation which is assumed in most cases, it does not happen when the amphiphilic species display large differences in hydrophilicity, as it is very common in commercial ethoxylated nonionic surfactants [1].

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In the case of non-collective behavior some species tend to preferentially migrate into the oil phase, others to the aqueous phase, and the remaining to the interface. In such a case, the individual behavior of each of the species is dictated by its partitioning coefficient K , which is defined as the ratio of its concentration in water C^w to its concentration in oil C^o in the absence of micelles. The K value is experimentally accessible by analytical means either from systems containing pure oligomers or commercial mixtures [2]. Since surfactant mixtures are used in many practical cases, this issue is quite important for formulation purposes, because what really matters as far as the properties are concerned is the composition of the mixture which is adsorbed at interface. All commercial ethoxylated nonionic surfactants exhibit a distribution in ethylene oxide number (EON), and thus include species which are quite different from one another as far as their affinity for oil and water is concerned. This complex case has been studied in detail in the past two decades by using the pseudophase model [3,4] to carry out an analysis of the partitioning between the excess phases of a Winsor III system [5–9].

The pseudophase approach has allowed to understand the behavior of complex mixtures, because it allows to calculate the interfacial mixture composition, which dictates properties such as interfacial tension or emulsion stability. In what follows the interfacial mixture is referred to as “real” surfactant mixture, in contrast with the “global” or “overall” mixture which is the one corresponding to the total system and is also called “apparent”. The corresponding formulation, i.e., the set of parameters which defines the balance between the hydrophilic and lipophilic affinities of the surfactant for the oil and water phases, will be referred to as interfacial formulation. The pseudophase model has permitted to explain not only the typical nonlinear behavior of a surfactant mixture, but also to resolve apparent contradictions like the case of the so-called retrograde transition in which an overall lipophilic surfactant mixture results in an apparent hydrophilic effect at the interface [10].

The partition coefficient has been determined for ethoxylated alkylphenol surfactants with linear [11] and branched [12] alkyl chains by measuring the concentrations in the excess phases of Winsor III systems. Its variation with temperature has been related to the surfactant affinity difference (SAD), a generalized formulation concept which measures the free energy of transfer of a surfactant molecule from oil to water [13].

This paper presents the principle of the pseudophase model and its utilization to calculate the interfacial physicochemical conditions, particularly the surfactant mixture average ethylene oxide number EON. It summarizes the state of the art on partitioning of ethoxylated surfactants with different oil and water phases, particularly n -alkanes [14] for which a linear mixing rule is found to represent the average behavior of oil mixtures [15,16], whereas it is not the case for oils containing polar or aromatic components [17,18].

This paper reports complementary new data on the effect of oil aromaticity on the partitioning of ethoxylated alkylphenol oligomers. It also reports experimental evidence on the ability of composition variables, i.e., surfactant concentration and water-to-oil ratio, to alter the interfacial surfactant mixture through a

change in partitioning, as predicted by the pseudophase model [5].

2. The pseudophase model to represent the interfacial surfactant mixture

The phase behavior of multiphasic SOW systems can be schematically described in terms of the so-called Winsor's types [19]: (1) Winsor's type I in which an aqueous surfactant-rich solution, which has eventually solubilized oil inside micelles, is in equilibrium with an excess oil phase, that contains surfactant at or below its critical micelle concentration (cmc). (2) Winsor's type II in which a surfactant-rich oil phase is in equilibrium with an aqueous phase that contains surfactant at or below its cmc. (3) Winsor's type III, i.e., a three-phase system in which a middle phase microemulsion containing most of the surfactant in a bicontinuous structure is in equilibrium with both excess oil and water. In all cases the phases are in equilibrium with the interface, whose physicochemical conditions dictate the tension and other interfacial properties.

Polyethoxylated nonionic commercial surfactants are mixtures containing a variety of oligomers, which have the same lipophilic part but a different number of ethylene oxide groups per molecule. The different oligomers can partition between the phases and the interface in different ways according to their individual affinity. Thus, the composition of the interfacial mixture, described as its average ethylene oxide number per surfactant molecule at interface (EON_{avint}), could be quite different from the total overall mixture average value (EON_{avT}) in the whole system.

The only currently available method to estimate the composition of the interfacial surfactant mixture is to use the so-called pseudophase model, which describes the equilibrium between the interface and the water and oil phases. This has been discussed in detail elsewhere [3–5], and only a simplified treatment is presented here.

The model is based on equality of chemical potential of the surfactant at the interface and in the water and oil phases. It is worth remarking that when one of the phases contains micelles, the chemical potential corresponds to the surfactant concentration which is outside the micelles. Since it is quite difficult to measure in practice the surfactant concentration outside the micelles, the best suited system to carry out experimental studies is the Winsor type III in which both excess phases are at or below the cmc [19].

In such three-phase system the pseudophase model is applied by assuming that the water and the oil which are in the microemulsion phase contain exactly the same surfactant mixtures as the corresponding excess phases [5]. According to this assumption, if all the water and oil contained in the microemulsion is (virtually) squeezed out of it, as indicated in Fig. 1 center scheme, the remaining (of the microemulsion) results in a surfactant mixture whose composition corresponds to the interfacial palissade so-called interfacial pseudophase, which is in equilibrium with the oil and water excess phases. This three-phase behavior is the case selected for the following discussion.

In the case of polyethoxylated phenol or alcohol surfactant mixtures, the subscript “ i ” indicates the degree of ethoxylation

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