



Partition coefficients of nonionic surfactants in water/*n*-alkane systems

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ABSTRACT

In water/oil systems, surfactants partition between the water phase and the oil phase according to their solubility in both phases. The ratio between the concentration of the surfactant in the oil phase and in the water phase at equilibrium is known as the partition or distribution coefficient (K_p). The partition coefficient (K_p) is an important fundamental parameter essential to understanding and controlling phenomena in water–oil–surfactant systems under both equilibrium and non-equilibrium conditions. In the present work we report on the partitioning of three different classes of nonionic surfactants in the pre-cmc regime, namely polyoxyethylene alkyl ethers (C_nE_j), alkyl dimethyl phosphine oxides (C_nDMPO) and alkyl glycosides (β - C_nG_m) between water and different *n*-alkanes. We focus on the influence of the surfactant's molecular structure (alkyl chain length, head group size and type), and oil chain length on K_p to derive systematic structure–property relationships. Moreover, we discuss the influence of the surfactant purity on partition coefficients of technical grade alkyl glycosides and polyoxyethylene alkyl ethers, respectively.

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1. Introduction

In water/oil systems, surfactants can be transferred from the water (oil) phase through the interface into the oil (water) phase in a diffusion-controlled process owing to the solubility of the surfactant in both water and oil until the equilibrium concentrations under the given conditions are reached. The ratio between the surfactant concentration in the oil phase and in the water phase under equilibrium conditions is known as the partition or distribution coefficient K_p . Partitioning was studied at pre-cmc surfactant concentrations [1–6] as well as above the cmc [7–11]. Depending on the regime investigated, different procedures and methods to determine the concentration of surfactant in water and oil at equilibrium conditions were applied. Ravera et al. [1] developed a procedure to determine the partition coefficient of surfactants using the surface tension measurements of surfactant solutions before and after equilibration with a defined volume of oil. However, this procedure cannot be used in the post-cmc regime since the surface tension of a surfactant solution will remain constant above the cmc, and depleting the aqueous phase due to transfer of surfactant into the oil phase will show no effect. To determine partition coefficients in the post-cmc regime, other analytical techniques such as HPLC and UV detection were therefore applied [7–9]. Recent stud-

ies in this regime focus on Winsor III type systems² with the aim to distinguish the deviation between the amount of surfactant adsorbed at the interface and the amount dissolved in the bulk phases [12].

Although the K_p value reflects the ratio of the equilibrium concentrations in the macroscopic phases it is closely related to dynamic transport phenomena taking place at the microscopic water/oil interface. For surfactants that possess a distinct solubility in both phases a coupling between adsorption to the interface and transfer of surfactant across the interface was found. The adsorption process could be described by taking into account the surfactant flux in the water phase and in the oil phase. Both the adsorption rate and the overall amount of adsorbed surfactant were found to be strongly dependent on the partition coefficient of the surfactant between the two phases, the diffusion coefficient in the phases, the volume ratio of the two solvents and thermodynamic interfacial parameters such as chemical potential and Gibbs free energy [1,2]. For dynamic processes such as relaxation of adsorption layers at water/oil interfaces it is essential to evaluate, understand and control the partitioning of surfactants in both phases [4,13]. This includes technical applications such as emulsification procedures, tertiary oil recovery, pharmaceutical, cosmetic and food applications as well as traditional detergency where non-equilibrium states play an important role [14,15].

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² Where a bicontinuous middle phase microemulsion coexists in thermodynamic equilibrium with a water excess phase and an oil excess phase.