

## Partitioning of Ethoxylated Octylphenol Surfactants in Microemulsion–Oil–Water Systems: Influence of Temperature and Relation between Partitioning Coefficient and Physicochemical Formulation

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The partitioning coefficient of a surfactant between oil and water is related to the free energy of transfer from one phase to the other. The influence of temperature on the partition coefficient of octylphenol ethoxylate oligomers between oil and water is reported. The variation of the partition coefficient with formulation variables can be used as a yardstick for the concept of generalized formulation expression.

### Introduction

Because of the synthesis reaction mechanism, commercial ethoxylated nonionic surfactants are a mixture of oligomers, sometimes with very different hydrophilicity, often with ethylene oxide chain length distributed according to a Poisson law.<sup>1</sup>

If the different species behave in some collective way, then some averaged property is attained for the surfactant mixture. This is actually the premise underlying the HLB mixing rules.<sup>2</sup>

However, this is not always true, because in some circumstances each of the species could tend to behave in an individual way. In these cases, the surfactant mixture composition is no longer the same at interface and in the bulk phases in equilibrium, so both the interfacial and micellar mixture compositions differ from the overall one.<sup>3,4</sup> In some extreme cases, some weird departure can take place, as in the so-called retrograde transition,<sup>5,6</sup> in which the introduction of an overall lipophilic surfactant mixture ends up in a hydrophilic effect.

The same non collective behavior of the oil molecules may affect the composition of the oil phase in the vicinity of the interface, as in the so-called lipophilic linker effect<sup>7–9</sup> and interfacial segregation.<sup>10</sup>

Surfactant mixtures are very broadly used in formulated products, and these phenomena may be considered to be only bothersome if they could be corrected by adjusting the formulation. However, in most cases they have to be curbed by increasing the surfactant concentration, with concomitant increased cost, toxicity, and environment pollution. Enhanced formulation practice would thus require the mastery of these mixture fractionation phenomena.

The pseudophase model was introduced to interpret the selective partitioning of the different oligomer species in surfactant–oil–water systems containing a commercial ethoxylated nonionic.<sup>11,12</sup> This model allowed the calculation of the interfacial oligomer composition from the overall system conditions. As a consequence, the true or interfacial formulation could be estimated. The model successfully predicted the experimental results, particularly the effect of surfactant concentration and water-to-oil ratio. It was also applied to more complex systems involving nonionic mixtures with anionic and cationic surfactants, and proved to be extremely useful.<sup>13,14</sup>

The pseudophase model requires the value of the partition coefficient of each surfactant species between the oil and aqueous phases, in the absence of micelles.<sup>11,15</sup> Original partitioning was measured at very low concentration, with the analytical limitation that this implies,

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