

Practical Surfactant Mixing Rules Based on the Attainment of Microemulsion–Oil–Water Three-Phase Behavior Systems

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Abstract Surfactant mixture are generally used to fine-tune formulations to an exact property value, such as changing its hydrophilicity. To do so a precise characterization method has to be used. The presented technique consists of the attainment of a microemulsion–oil–water Winsor III three-phase behavior in a reference system. It allows one to classify surfactants in a hydrophilicity scale with an accuracy equivalent to one tenth of HLB unit. The characterization method is applied in different ways, including simple and double scans, to an unknown surfactant and to mixtures of two base surfactants. It is also used to test the ideality of the mixing rule expression, which is equivalent to a linear variation of the characteristic parameter versus the mixture composition. Conditions for linearity of the mixing rule are discussed. The selective partitioning of different species results in non-linear mixing rules, whose detection is discussed according to the aspect of the three-phase region in different diagrams. Typical mixing rules for pH sensitive systems containing fatty acids and fatty amines are shown. Anionic–nonionic mixtures are found to exhibit a slight deviation from ideality. The special case of antagonistic anionic–cationic mixture is shown to be easily linearized by introducing a virtual, catanionic species.