

Application Report

Characterization of surfactants

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Force Tensiometer – K12

Method:



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Critical micelle concentration as a function of head group size for alkyl alcohol ethoxylates

Background

Nonionic surfactants are of utmost importance in many commercial and industrial products. These compounds act as cleaners, dispersants, emulsifiers, and defoamers just to name a few applications. One of the largest advantages of nonionic surfactants in product formulations is that, since they are non-electrolytic, their properties are largely resistant to changes in system pH and electrolyte content. In addition nonionic surfactants are generally compatible with ionic surfactants, neutral polymers, and polyelectrolytes.

Alkyl alcohol ethoxylates are among the most commonly used nonionic surfactants. These compounds are synthesized via the reaction of an alkyl alcohol with ethylene oxide to form a surfactant with an alkyl tail (hydrophobic) group and a polyethyleneoxide head (hydrophilic) group. The physical/chemical properties of alkyl alcohol ethoxylates are largely dependent on the specific and relative lengths of their head groups and their tail groups. For example alkyl alcohol ethoxylates with low degrees of ethoxylation (2 to 5 ethylene oxide units in the head group) are generally only oil soluble. They are commonly used as degreasers and fiber lubricants in a variety of industries. On the other hand, alkyl alcohol ethoxylates with high degrees of ethoxylation (7 to 20 ethylene oxide units in the head group for example) are generally water soluble. These surfactants are often used as oil-in-water emulsion stabilizers and wetting agents.

One of the great challenges in the synthesis of alkyl alcohol ethoxylates is to precisely control the extent and distribution of ethoxylation to produce surfactants with the desired physical/chemical properties. A number of catalysts and processing techniques have been developed for this purpose. A strongly related analytical/quality control problem is to identify a facile physical technique which can be used to quantify the extent of ethoxylation obtained from a given synthesis with respect to some benchmark of surfactant performance.

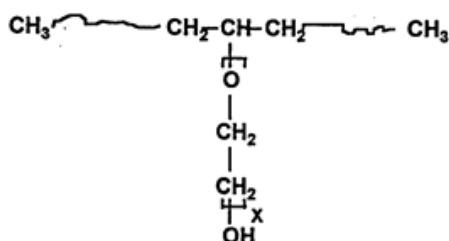
One of the most commonly cited benchmarks of a surfactant's physical/chemical properties is the surfactant's critical micelle concentration. The critical micelle concentration (CMC) is the point in concentration at which it becomes thermodynamically favorable for surfactant molecules in solution to form aggregates (micelles) in order to minimize the interaction of either their head groups or their tail groups with the solvent. For alkyl alcohol ethoxylates in aqueous solution micellization is due to entropic considerations. Water molecules in close proximity to the hydrophobic tail groups of the surfactant molecules take

on a certain ordered configuration, which is entropically unfavorable. Once the surfactant concentration reaches a certain level (the CMC) the water structure forces aggregation of the hydrophobic tail groups- thus forming surfactant micelles.

As the extent of ethoxylation is increased for alkyl alcohol ethoxylates (with the alkyl chain length being held constant), the CMC increases. In other words, since surfactants with larger head groups are more hydrophilic, a larger concentration of them in solution is necessary for micelle formation to become thermodynamically favorable. This application note focuses on the use of surface tensiometry to determine CMC values for alkyl secondary alcohol ethoxylates. It further suggests that surface tensiometry can be used as an analytical/quality control technique to characterize the extent of ethoxylation achieved in syntheses of alkyl alcohol ethoxylates and, more generally, the head group size in surfactants with polymeric head groups.

Experimental

The critical micelle concentrations for a series of alkyl secondary alcohol ethoxylates have been determined by surface tensiometry. These alkyl secondary alcohol ethoxylates have the following general chemical structure:



The manufacturer of these surfactants reports that the alkyl tail groups are linear and that all of the surfactants studied here have a distribution of alkyl carbon chain lengths in the range of 11 to 15 carbons. The average length of the ethyleneoxide head group is variable throughout the series of surfactants. Five surfactants were studied with average ethyleneoxide lengths of $X = 7.3, 8.9, 12.3, 15.5,$ and 20.1 , as determined by independent methods. The surface tensions for aqueous solutions of variable surfactant concentration were determined using the Krüss model K12 processor tensiometer. The K12 was equipped with an automated dosing accessory so that surfactant concentration was incremented automatically. The Wilhelmy plate technique using a platinum plate was employed.

Results and discussion

Figure 1 shows surface tension versus concentration data for each of the five alkyl secondary alcohol ethoxylates studied.

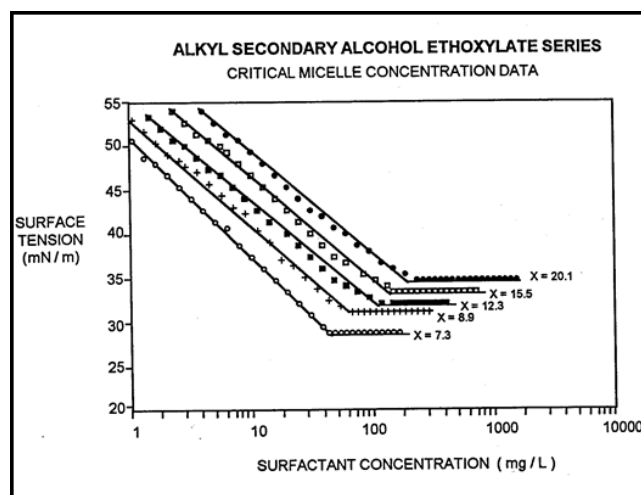


Figure 1

At sub-CMC concentrations, for each of the surfactants, surface tension decreases with increasing surfactant concentration. This is due to the adsorption of surfactant to the air/water interface. At the CMC for each surfactant, surface tension becomes relatively independent of further concentration increases. It becomes more thermodynamically favorable for the surfactant molecules to form micelles rather than to further adsorb at the air/water interface in response to concentration increases. In terms of chemical potential the air/water interface is saturated with surfactant at the CMC. A CMC value for each of the surfactants studied has been obtained from figure 1 as the point in concentration at which each curve undergoes a distinct change in slope.

As expected, throughout the series of surfactants studied the CMC value increases with increasing extent of ethoxylation. Figure 2 is a plot of average extent of ethoxylation versus CMC for this series of surfactants. Such data was curve fitted quite easily.

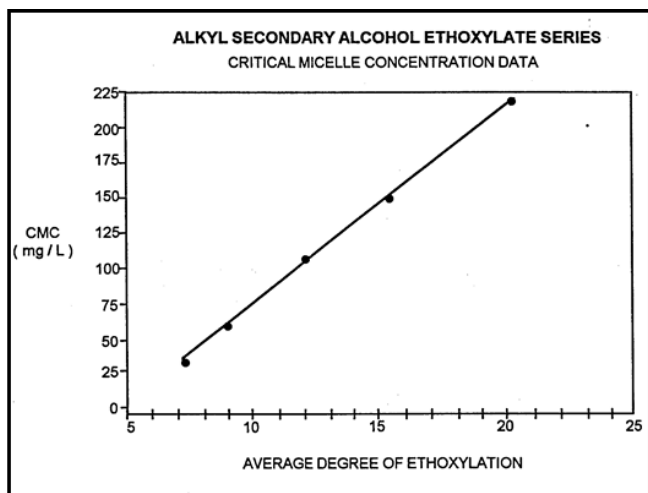


Figure 2

The analysis which figure 2 provides leads to the concept that once a series of alkyl alcohol ethoxylates, for which the extents of ethoxylation have been well characterized by other methods, has been studied by surface tensiometry then surface tensiometry can be used as an independent analytical/quality control technique to evaluate the extent of ethoxylation in subsequent syntheses. The value of surface tensiometry in this regard is two-fold. First, surface tensiometry is generally a more facile technique versus chromatography, elemental analysis, and other techniques, which may be used to determine the extent of ethoxylation in these surfactants. Second, and perhaps more importantly, apart from providing a quantitative evaluation of the chemical structure of the surfactant in question, surface tensiometry provides a quantitative interpretation of the physical properties of the surfactant. The CMC is the point in concentration above which a surfactant has the opportunity to be an effective emulsifier for oils or stabilizer for disperse insolubles for example. Other analytical techniques which focus purely on evaluating chemical structure provide little information regarding the actual utility of the surfactant in question.

Conclusions

Through the study of a series of alkyl secondary alcohol ethoxylates it has been shown that surface tensiometry can be an effective analytical/quality control technique in the evaluation of surfactant chemical structures and physical properties. One can certainly envision the extension of the techniques discussed in this note to the evaluation of other nonionic surfactants which are synthesized with polymeric head and/or tail groups. Such surfactants include alkylpolyglycosides, polyoxyethylenated silicones, and ethylene oxide/propylene oxide copolymers. Applications to the quantification of extents of reaction in the synthesis of ionic surfactants might also be envisioned.