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Article For Cosmetics & Toiletries Magazine (Formulators Forum)
July 10, 2001

Alkanolamides...Revisited!

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In the last few years several raw material suppliers have developed materials intended to replace alkanolamides in surfactant-based products. The reason for this goes back to some "bad press" that has been swirling around these materials for several years. I even heard a buyer from a very large chain drug store say that his company would not sell (their store brand) if it contained "cocamide DEA," but further questioning revealed that he had no problem at all with "lauramide DEA." In reality both designations can describe the same product, since the predominate chain length in coco is lauric(C₁₂)!

Ask any formulator of shampoos or body washes what is the function of alkanolamides, and I'm sure you will get the same response: "they are

thickeners and foam boosters." Actually, neither statement is true! They modify the position and shape of the salt curve and they can (sometimes) stabilize the foam, but they rarely boost foam. So, why do formulators have such misconceptions about these materials that have been available and widely used for decades? Before we delve into this question, let's spend a few moments dealing with the chemistry of alkanolamides.

Kritchevsky, who worked for the Stepan Company, first developed these functional materials. (A bit of trivia: The first alkanolamides were sold under the trade name "Ninol" because Kritchevsky's daughter was named Nina!) The first alkanolamides were made by reacting two moles of an amine (diethanolamine) with one mole of a fatty acid (lauric acid).

Materials made via this approach (2:1 ratio are known as Kritchevsky Amides). This reaction yielded one mole of alkanolamide (see below) and one mole of amine soap. The presence of the amine soap accounted for the high pH of this product along with a high free amine content. Additionally, these materials had good water solubility (depending on chain length) and could actually boost foam.



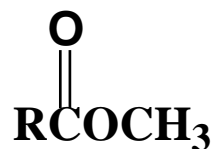
Actually the starting fatty material can be a fatty acid, a triglyceride or a methyl ester. When a fatty acid is used the by-product is water, which is stripped off. When a triglyceride is used three moles of the alkanolamide is produced along with glycerin (which can lower the viscosity of the finished

product). Additionally, the presence of glycerin causes the alkanolamides to be liquid at room temperature (depending, once again on the fatty chain length). When the reactant fatty material is a methyl ester, one mole of alkanolamides is produced along with methanol, which is stripped off and sold. When the ratio of fatty (acid) material to amine is 1:1, we have the "Superamides." Which are generally solids, depress the foam and are water insoluble. Another point to consider is the nature of the amine used to react with the fatty moiety. While generally diethanolamine is most often seen, in recent years we have seen a dramatic rise in the use of monoethanolamine. Monoethanolamides have higher melting points than their diethanolamine relatives, and will have a more dramatic effect in "building" viscosity. While minoisopropanolamine can also be used, it seldom is due to the fact that the resulting amide has a melting point often above 70C. Today, the vast majority of alkanolamides used in the US are of the Super amide type. In addition to the alkanolamide there can be several byproducts of the synthesis reaction present:

Amide ester



Amine ester



Reactant ester (methyl ester)



The presence of each of these materials will seriously degrade the performance of the alkanolamide by further reducing foam, raising the cloud point and making it very difficult to produce a clear finished product.

Another possible source of difficulty may be the presence of unreacted starting "fatty" material, such as fatty acid or triglyceride. These will cause similar problems to the esters.

In order to understand the functionality of alkanolamides let's discuss the factors that effect the viscosity, foaming and clarity of shampoos (surfactant systems). When we add a surfactant to water it will exhibit a CMC (critical Micelle Concentration). The first drops (molecules) of surfactant migrate to the air/water interface so that they can orient their fatty tails into the air and away from the water (which "hates" the fatty tails). Very quickly the surface is saturated with surfactant and the "excess" surfactant forms spheres (micelles) where the fatty tails orient toward the center (away from the bulk water) with the polar groups (usually negatively charged-anionic) facing outside (toward the bulk water). If we add additional fatty material, it will get entrapped into the center of the surfactant micelles which swells them and thus the viscosity increases. A good example of this is seen when "old-time" chemists would add small amounts of lauryl alcohol to build viscosity. It was quite effective but often resulted in a hazy/cloudy shampoo. Adding alkanolamide to a surfactant system can have a similar effect. Keep in mind that alkanolamides are quite water insoluble and will be incorporated into the surfactant micelles (swelling them). Most chemists believe that alkanolamides are water soluble since they appear so when added to the "shampoo", but don't consider that they are being solubilized by the surfactant. Have you ever added a highly concentrated surfactant to water only to see areas of gellation form that were most difficult to eliminate through normal processing? I know I have! What actually happened was that the concentrated surfactant "grabbed" onto the available water to form a

liquid crystalline gel network. Sometimes this gel network can form the dreaded hexagonal liquid crystals which can be almost impossible to eliminate with conventional mixing. However, by adding an alkanolamide, you can change the structure of the gel network and eliminate the pesky gellation. Actually, the alkanolamide acts like a Hydrotrope (it really isn't a Hydrotrope, which has a large head group and virtually no fatty tail) and promotes curvature at the interface which destroys the gel network.

Another important concept that is necessary to understand is that of salt curve. As we add salt (generally sodium chloride) to a surfactant solution the viscosity increases gradually. The reason for this increase is due to two separate and competing factors. The electrolyte increases the effective size of the surfactant micelles and the viscosity increases. Secondly, the electrolyte competes with the surfactant for water. Thus as we add electrolyte the system "thinks" we have increased the concentration of the surfactant and the viscosity increases. As we add more electrolyte we upset the charge balance around the micelles and very quickly the viscosity decreases. This explains the commonly seen shape of the salt curve. When we add alkanolamide to the surfactant solution, the viscosity increases. But actually what has happened, is that the salt curve has been shifted to the left. Thus less salt is needed to increase the viscosity. Often, the maximum achievable viscosity is lower than what can be achieved without alkanolamide. However, if we add a high concentration of salt we will increase the cloud point and an unacceptable product will result! Another factor to consider is fragrance Solubilization. If the formulator wants to incorporate fragrance at any level above 0.25% use of an alkanolamide will greatly facilitate this! It may be theorized that alkanolamides accomplish this task of fragrance coupling by matching the solubility parameter of the fragrance to the shampoo base and thus achieve a clear product.

Finally, since alkanolamides are rather poor surfactants (their polar end is not very polar compared to their fatty end), they tend to depress foam. However, in many cases they can stabilize the foam by gelling the water at the foam/air interface and thus increase the time it takes for water to drain from the bubble and improve foam stability.

Alkanolamides have been around for many years and yet we are still learning just how versatile they are.