SHORT COMMUNICATION

Effects of Branching upon Some Surfactant Properties of Sulfated Alcohols

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ABSTRACT: A study was undertaken to determine the surfactant properties of various sulfated alcohols. Most notably, the Krafft point and the ability to emulsify decane were studied. A series of sulfated Guerbet alcohol and Guerbet alcohol alkoxylate sulfates with 16 carbon atoms and an analogous series based upon cetyl alcohol, a linear C_{16}, were studied as hydrophobes.

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KEY WORDS: Cetyl alcohol, emulsification, ethoxylation, Guerbet alcohol, Krafft point, sulfation.

Sulfated surfactants are known to be good emulsifiers for a variety of applications. The most basic structural requirements for a molecule to be surface-active are a water-soluble portion (the hydrophilic portion) and a water-insoluble portion (the hydrophobic portion). The balance between these two portions is the key to the functional attributes of the molecule. We also believe that branching and other structural alterations change the emulsifying ability of a surfactant.

Sulfation chemistry. The term alcohol sulfate refers to any product that has an SO_4 group linked to a fatty moiety. The linkage is carbon to oxygen to sulfur. This distinguishes the class from the sulfonate group, which has an SO_3 in which the carbon is directly linked to the sulfur group. The alcohol sulfate can be hydrolyzed at low pH to obtain an alcohol and an inorganic sulfate. Sulfonates are stable in acid. These sulfates are shown in Table 1.

Due to the simple equipment requirements and ease of preparation, we chose chlorosulfonic acid sulfation for our study, because of the degree of reaction obtained and the ease of handling in the lab.

HYDROPHOBES STUDIES

Guerbet alcohols. Guerbet alcohols have been known since the 1890s when Marcel Guerbet (1) first synthesized these materials. The reaction sequence that bears his name is related to the aldol reaction and occurs at high temperature under catalytic conditions. The overall reaction can be represented by the following equation:

$$2\,RCH_2CH_2OH \xrightarrow[\text{Catalyst}]{} \underset{\displaystyle RCH_2CH_2\!\!\mid}{RCHCH_2OH} + H_2O \qquad [1]$$

where *R* is alkyl. The product is an alcohol with twice the molecular weight of the reactant alcohol minus a mole of water.

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TABLE 1
Sulfating Agents

Sulfamic acid	Chlorosulfonic	Sulfur trioxide
Approximate conversions		
93%	95%	97%
Advantages		
Mild reaction	Moderate reaction	Aggressive reaction
Few by-products	Good conversion	Good conversion
Disadvantages		
Ammonium salt requirements	HCl by-product	Equipment requirements
Lower conversion products	No AOS[a]	Many by-products
	Some aromatic reaction	

[a]Alpha olefin sulfonate.

PROPERTIES

Guerbet alcohols used in our study have the following properties: (i) Because they are branched, they are liquid at lower temperatures than their linear counterparts (Fig. 1); (ii) they have low volatility; (iii) they are primary alcohols, hence are reactive and can be used to make many derivatives; (iv) they are useful as super fatting agents to re-oil the skin and hair; and (v) they are good lubricants.

The Guerbet alcohols studied are essentially saturated, hence: (i) They exhibit good oxidative stability, as shown by good Gardner colors, both initially and at even when stored at elevated temperatures; and (ii) they exhibit improved color stability over unsaturated products in many formulations.

Guerbet alcohols per se are useful in many applications (2–8). They are primary alcohols, with a high degree of regiospecific beta branching.

A sixteen-carbon Guerbet alcohol was chosen for evaluation. It conforms to the following structure and has the Cos-

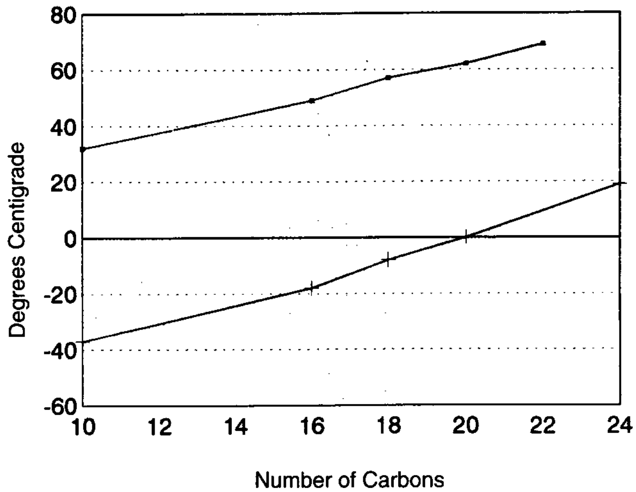

FIG. 1. Melting points of linear (□) and Guerbet (+) alcohols.

metics, Toiletries and Fragrance Association name hexyldecanol (Eq. 2). It is commercially available from Vista Chemical Company (Houston, TX).

$$CH_3\text{-}(CH_2)_7\text{-}\underset{\displaystyle CH_3(CH_2)_4CH_2}{\underset{|}{CH}}\text{-}CH_2\text{-}OH \qquad [2]$$

The alcohol was ethoxylated and/or propoxylated, then sulfated as described in the next section.

Cetyl alcohol. Fatty alcohols of natural origin are straight-chain, even-carbon, primary alcohols. We confined our studies to high-purity (95+%), natural linear alcohols. Specifically, we evaluated: cetyl alcohol (C_{16}) from Vista.

Krafft point analysis. The Krafft point, a measure of water solubility, is defined as the temperature at which a 1% dispersion becomes clear under gradual heat. The Krafft point will increase with the molecular weight of the sulfated hydrophobe (Table 2), or as one adds propylene oxide to the hydrophobe. The Krafft point decreases with addition of ethylene oxide to the molecule (Table 3).

The Guerbet derivatives with their high molecular weight and branching have high Krafft points. The addition of ethylene oxide will lower the Krafft point (i.e., the material becomes more water-soluble).

TABLE 2
Krafft point (°C) of Linear Alcohol Sulfates

Description	Number of carbons	Krafft point
Sodium lauryl sulfate	12	16
Sodium myristyl sulfate	14	28
Sodium cetyl sulfate	16	45
Sodium stearyl sulfate	18	56
Sodium oleyl sulfate	18	29
Sodium salt of sulfated octyldodecanol	20	Insoluble

TABLE 3
Krafft point (°C) Ethoxylated Linear alcohol Sulfates

Description	Number of carbons in hydrophobe	Krafft point
Sodium cetereth-3-sulfate	16	19
Sodium cetereth-2-sulfate	16	24
Sodium steareth-3-sulfate	18	32
Sodium steareth-2-sulfate	18	40
Sodium oleth-3-sulfate	18	26
Sodium oleth-2-sulfate	18	40
Sodium salt of sulfated 3 mole EO[a] on octyldodecanol	20	Insoluble
Sodium salt of sulfated 5 moles EO on octyldodecanol	20	Insoluble
Sodium salt of sulfated 12 moles EO on octyldodecanol	20	91
Sodium salt of sulfated 15 moles EO on octyldodecanol	20	58
Sodium salt of sulfated 20 moles EO on octyldodecanol	20	0

[a]EO, ethylene oxide.

ABILITY TO EMULSIFY OIL

A study was undertaken to determine the effect of branching upon the ability to emulsify oil. Because the emulsifying ability is affected by the presence of salt (NaCl), its concentration was also varied to determine the maximum amount of oil that could be dissolved. Each surfactant was studied to determine the maximum percentage of oil emulsified and the level of salt needed to emulsify that level of oil. Decane was chosen as the standard oil.

The sulfates tested were sodium salts, all adjusted to 25% actives. They had been sulfated with chlorosulfonic acid. Active surfactant, based upon total weight of decane and water, was added at 2% to all test cylinders.

Emulsification test method. Decane (30 mL) and 26 mL water, containing the desired amount of sodium chloride, were introduced into a graduated cylinder. Surfactant (4.8 g @ 25% active) was then added. The cylinder was sealed and shaken. The cylinder was placed in a water bath at 50°C for 24 h and checked for volume of oil (top phase), volume of emulsion (middle), and volume of water (bottom). The percentage of oil and water in the emulsion is then easily ascertained.

Two factors were determined—the amount of salt concentration required for maximum emulsification of oil, and how much oil was emulsified per unit of surfactant (Table 4).

Optimized salt concentration. Table 4 shows the salt concentrations at which the surfactants emulsify the most oil. The linear products require more salt than the Guerbet derivatives to reach maximum emulsified oil. The Guerbet alkoxy sulfates require between 3 and 6% salt for optimum performance. The linear products require between 7 and 18%.

We can conclude that: (i) The introduction of unsaturation into the hydrophobe, used in the preparation of sulfates or ethoxy sulfates, results in a product that has a lower Krafft point than if a linear alcohol with the same number of carbon atoms was sulfated. The 20-carbon Guerbet sulfate is insolu-

TABLE 4
Salt Concentration Required for Maximum Oil Emulsification and Amount of Oil Emulsified per Gram of Surfactant.

Surfactants tested	Optimum salt concentration (% NaCl)	Grams decane emulsified per gram of surfactant used
C_{16}-3-PO[a] sulfate sodium salt	9.0	12.0
C_{16}-4-PO sulfate sodium salt	7.5	6.0
C_{16}-6-PO sulfate sodium salt	3.5	4.0
C_{16}-3-EO[b] sulfate sodium salt	16.5	5.7
C_{16}-4-EO sulfate sodium salt	18.5	4.8
Guerbet 16-2-EO sulfate sodium salt	3.0	8.3
Guerbet 16-3-EO sulfate sodium salt	4.0	8.8
Guerbet 16-4-EO sulfate sodium salt	5.5	16.0

[a]PO, propylene oxide.
[b]EO, ethylene oxide.

ble in water, unlike either the unsaturated oleyl sulfate or saturated linear sulfate, which has a Krafft point. To get a comparable Krafft point for a 20-carbon Guerbet ethoxy sulfate as for the linear saturated 18-carbon sulfate, one needs to add 15 moles of ethylene oxide prior to sulfation. Guerbet alcohols are highly hydrophobic.

(ii) Linear hydrophobes, when ethoxylated and sulfated, exhibit lower Krafft points than nonethoxylated materials. The more ethylene oxide added, the lower the Krafft point. This is not surprising because addition of ethylene oxide to hydrophobes makes the resulting sulfate more water-soluble.

(iii) Guerbet hydrophobes, when ethoxylated and sulfated, exhibit lower Krafft points than the nonethoxylated materials, just like the linear materials. However, to obtain a similar Krafft point, Guerbet alcohols need much more added ethylene oxide. Stated differently, Guerbet alcohols are much more hydrophobic at the same carbon length than are linear alcohols.

(iv) The oil emulsification study indicated that the incorporation of branching into the molecule had a beneficial effect upon the amount of oil that could be emulsified. When branching is introduced *via* reaction of the hydrophobe with propylene oxide, there is a maximum effectiveness at about three moles of propylene oxide. Increasing the amount of propylene oxide to four or six moles results in a decrease in the amount of oil emulsified. We speculate that about three moles of propylene oxide are needed to react with the majority of the hydroxyl groups; after that, the hydroxyl groups are all secondary.

(v) Incorporation of three moles of ethylene oxide onto linear alcohol, prior to sulfation, results in a product that emulsifies about one-half of the oil, as does incorporation of the same number of moles of propylene oxide.

(vi) If a Guerbet alcohol, which is branched, is ethoxylated to four moles of ethylene oxide prior to sulfation, it results in a sulfate with outstanding emulsification properties. The Guerbet ethoxy sulfate with four moles of ethylene oxide emulsifies more oil than the linear propoxy sulfate with four moles of propylene oxide, and much more oil than the linear ethoxylate. Again, the Guerbet alcohol has very unusual properties in oil emulsification.

(vii) The Guerbet alkoxy sulfates, in addition to being good emulsifiers, require less salt to optimize the amount of oil emulsified.

Guerbet alcohols are unique branched hydrophobes and give rise to a series of unique surface-active agents. This uniqueness is related to water solubility, as measured by Krafft point and emulsification.

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