Anionic Interactions with Cationic Gemini Surfactants

Tony O'Lenick

Siltech LLC, Dacula, Ga., USA

Thomas G. O'Lenick

University of Tennessee, Knoxville, Tenn., USA

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The objective of this paper is to expand the study of **ABSTRACT:**

interactions between anionic and cationic surfactants to specific gemini surfactants and to investigate whether their interactions depend upon the linkage

group between them.

Relatively few new classes of materials have come into existence since the first surfactant was formulated into a product. Recently, gemini surfactants have drawn increasing attention and commercial success. Originally, the term gemini surfactant was coined to describe a dual hydrophobic tail surfactant. It subsequently has been expanded and applied to a number of multiple-head surfactants. This article looks at some of the properties of gemini surfactants with differing flexibility of the linkage groups. These surfactants have been shown to exhibit superior properties in terms of wetting and emulsification at very low concentrations when compared to traditional surfactants.

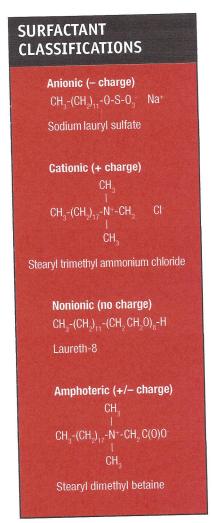
The rigid gemini surfactant was the hardest of the series, showing a marked incompatibility with SLS.

Background

One of the many methods of dividing surfactants into groups is based on the charge on the organic portion of the molecule. According to this scheme, surfactants fit into one of the following classifications: anionic (negatively charged), cationic (positively charged), nonionic (without a charge), or amphoteric (positively and negatively charge)—see Surfactant Classifications.

These materials are used in a variety of formulations and rarely are used alone. A look at a typical shampoo bottle will show numerous materials that make up a formulation. The functionality of the shampoo depends not only on the nature of each ingredient in the formulation, but also on the interactions between the ingredients. It is these interactions that provide, among other things, optimum detergency, foam, wetting and viscosity. The consumer's perception of the attributes given to a product makes for its success or failure on the market. Consequently, it is important for formulators to understand the interactions occurring between ingredients.

The interaction between anionic and cationic materials generally is understood. When stearalkonium chloride and sodium lauryl sulfate are mixed together, a white, gunky paste results. The nature of this interaction, and the interaction of cationic and anionic surfactants, has



been investigated in a previous article.1 In that work, hard and soft quats were defined. Hard quats were incompatible with anionic surfactants. Soft quats, on the other hand, were quats that formed thick, clear, high-foaming complexes with anionic surfactants. Differences also were found in the hardness of the anionic surfactants: sodium laureth-2sulfate (SLES-2) was found to be more compatible with quats than sodium lauryl sulfate (SLS).

The objective of this paper is to expand the study of interactions to specific gemini surfactants and to investigate whether their interactions depend upon the linkage group between them.

Gemini Surfactants

Generally, conventional surfactants have one hydrophilic group and one hydrophobic group. However, a recent class of compounds having at least two hydrophobic groups and at least two hydrophilic groups has been introduced. This class has become known as the gemini surfactants, with much of the pioneering work carried out by M. Rosen, Ph.D.² While there are earlier references to compounds having at least two hydrophilic groups and at least two hydrophobic groups, they were not referred to as gemini surfactants until 1993.3

Recently, B. S. Sekhon⁴ described gemini surfactants: "A gemini surfactant (GS) consists of two conventional surfactant molecules chemically bonded together by a spacer. The two terminal hydrocarbon tails can be short or long; the two polar head groups can be cationic, anionic or nonionic; the spacer can be short or long, flexible or rigid. The GS need not be symmetrically disposed about the center of the spacer. GSs can selfassemble at much lower concentrations and are superior in surface activity as compared to conventional surfactants. GSs are attractive for catalysis and adsorption applications, new synthetic vectors for gene transfection, analytical separations, solubilization processes, nanoscale technologies, biotechnologies, enhanced oil recovery and as paint additives."

The micellization behavior of gemini surfactants is qualitatively different from that of conventional surfactants. The lower critical micelle concentration (CMC) can be attributed directly to the increase in the number of hydrocarbon groups in the molecule. The CMC of gemini surfactants is a nonmonotonous function of the number of spacer hydrocarbon groups, with a maximum value of approximately 4-6 polymethylene groups. Furthermore, in the case of ionic gemini surfactants, the spacer reduces the intermolecular repulsion between the head groups. This leads to micelle formation at low CMC values in gemini surfactants.

Gemini surfactants generally are superior to conventional surfactants in terms of surface activity. This is due to the distortion of the hydrophobic groups by water. Gemini surfactants are twin surfactants having symmetrical charges and hydrophobic groups linked by a so-called linkage group. The two hydrophobic groups in a single molecule are more disruptive than the individual chains in conventional surfactants. This property promotes the migration of micelles to the air/water interface.

Gemini surfactants also can be used in smaller quantities than conventional surfactants.4 Gemini surfactants have been found to be effective emulsifiers when used at very low concentrations. This superior detergency at lower concentrations has drawn increased interest in recent years.

Understanding Gemini Surfactants

Common properties of both gemini and traditional surfactants were examined and compared. The specific gemini surfactants chosen for study included rigid bridge gemini surfactants (Figure 1), flexible bridge gemini surfactants (Figure 2), and non-gemini surfactants (Figure 3).

One of the top interests in gemini surfactants is the alpha-omega $(\alpha$ - $\omega)$ arrangement of their hydrophobic groups and what this arrangement means at the surface of water.

A traditional surfactant will orientate itself at the surface of the water with the polar head in the water and the oil-soluble tail out of the water. The reason for this arrangement is to obtain a state of minimum free energy. With the surfactant so orientated, the minimum number of hydrogen bonds is distributed between water molecules and the lowest free energy is obtained.

Considering the gemini surfactant, the hydrophobic tails cannot simply rotate out of the water to obtain minimum free energy. In order for both hydrophobic tails to rotate out of the water to obtain minimum free energy, the molecule must at least bend into a hairpin configuration. This results in a significantly different aqueous solution than traditional surfactants. It also should be clear that as the bridge group becomes more and more flexible, the ease of obtaining a low-energy hairpin is increased.

Interest has grown in the interaction of cationic and amphoteric surfactants with anionic surfactants in aqueous solution to allow the formulation of clear conditioning systems. The terms hard and soft quats have been proposed based on compatibility of the quat with anionic surfactants. Soft quats are soluble and form a gel with anionic surfactants at near stoichiometric concentrations. Gemini surfactants offer a new class of compounds to potentially improve solubility of the anionic/cationic complex. An additional aspect of such complex solubilization is the bridging group. The alteration of the bridging group used in gemini surfactants should have a dramatic impact upon the hardness of a gemini quat, as this paper will investigate.

$$\begin{array}{cccc} {\rm CH_3} & {\rm CH_3} \\ {\rm I} & {\rm I} \\ {\rm R-N^+-CH_2CH(OH)CH_2-N^+-R} & {\rm 2CI^-} \\ {\rm I} & {\rm I} \\ {\rm CH_3} & {\rm CH_3} \end{array}$$

Figure 1. Rigid bridge gemini surfactant

Figure 2. Flexible bridge gemini surfactant

Figure 3. Non-gemini surfactants—glyceryl quat

Anionic Surfactants

The anionic surfactants studied were SLS (designated as S-1)^a and SLES-2 (designated as S-2)^a. Their structures are shown in Figures 4 and 5, on page 59.

Foam Conclusions

The foam of the gemini surfactant by itself in water shows an interesting dependence upon structure. Table 1 and Figure 6, both on page 60, show the results of foam evaluation using the standard Ross Miles Foam test.

In the case of the coco compounds studied, the flexible bridge gemini surfactant had the highest foam of the series in both the 3- and 5-min time frame, despite lower initial foam. The non-gemini surfactant had the best initial foam in the coco series. In the

^a Surfactants studied were commercially available from Colonial Chemical, So. Pittsburg, Tenn., USA.

Figure 4. Sodium lauryl sulfate (SLS)

case of the castor compounds studied, the glyceryl compound performed better than either gemini surfactant at all times studied.

Anionic Compatibility

A study of the compatibility of cationic materials and SLS and SLES-2 was conducted. The anionic compounds were diluted to 10% active with water. The cationic compounds were likewise cut to 10% active with water. In addition, 10% active quat was titrated to 100 g of 10% active anionic surfactant.

The viscosity was measured using a viscometer and spindleb,c. During the addition of the quat to the SLS and SLES-2 the solution gels and thickens; after the mixture settles, the gel becomes softer.

SLS Results

Compatibility with SLS was independent of the alkyl group studied (see Table 2, on page 61, and Figure 7, on page 62). The rigid quat had the most incompatibility with SLS. The glyceryl (non-gemini) quat had the next best compatibility, and the flexible gemini was infinitely compatible. In other words, the rigid gemini surfactant was the hardest of the series, showing a marked incompatibility with SLS. The

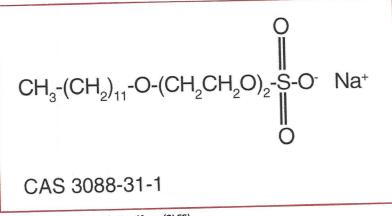


Figure 5. Sodium laureth-2-sulfate (SLES)

b Brookfield Syncro-lectric viscometer is a product of Brookfield Engineering Inc.

^c Brookfield Syncro-lectric spindle LV 3 and LV 2 are products of Brookfield Engineering Inc.

glyceryl compound was more polar and softer, thus more compatible with the SLS. The flexible gemini compounds were soft quats, compatible with SLS over a wide range.

SLES-2 Results

Compatibility with SLES-2 was independent of the alkyl group studied and similar to that observed with SLS (see **Table 3** and **Figure 8**, both on page 63). The rigid quat had the most incompatibility with SLES-2. The glyceryl (non-gemini) quat had the next best compatibility, and the flexible gemini was infinitely compatible. In other words, the rigid gemini surfactant

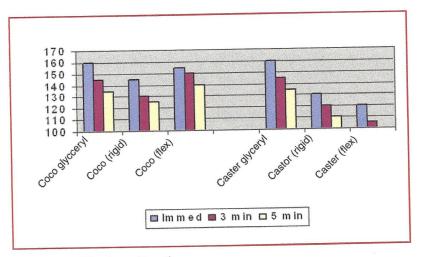


Figure 6. Ross Miles foam, 1% active

Product	Coco HP (rigid)	Coco PEG DHP (flex)	Coco Glyceryl (non-gemini)	Castor HP (rigid)	Castor PEG DHP (flex)	Castor Glyceryl (non-gemini)	Coco/Cast or PEG (flex)
T 1	1/5	155	160	130	120	160	145
Immed	145	150	145	120	105	145	135
1 min 5 min	130 125	140	135	110	100	135	130

was the hardest of the series, showing a marked incompatibility with SLES-2. The glyceryl compound was more polar and softer, i.e., more compatible with the SLES-2. The flexible gemini compounds were soft quats, compatible with SLES-2 over a wide range.

Foam and Wetting Properties

Table 4, on page 63, and **Figure 9,** on page 64, show Ross miles foam data and Draves wetting data on quat titra-

tions with SLS @ 1% active @ 25.0°C.

The coco glyceryl quat was insoluble in SLS combination and provided no foam. It was a hard quat with SLS. The castor glyceryl material was softer and provided foam. Regardless of the alkyl group, the foam height followed the following order: Glyceryl < Flexible < Rigid

Quat Combination Foam

Ross Miles foam data and Draves wetting data on quat titrations with

SLES-2 @ 1% active @ 25.0°C is shown in **Table 5**, on page 64, and **Figure 10**, on page 65.

The coco glyceryl quat was insoluble enough in SLES-2 combination as to provide marginal foam, as opposed to no foam for the SLS. It was a hard quat, but the SLES-2 was a softer anionic than SLS. The combination was therefore somewhat more soluble and provided marginal foam. The castor glyceryl material was softer and

SLS	Quat sample	Grams added to haze point	Viscosity @ 21.5∞C	Notes
	6 UD (: : : N	43.5	155	Gel formed during addition
	Coco HP (rigid)	Soluble to a 1:1 ratio 83.0 30.9 Soluble to a 1:1 ratio	44	No gel formed, no haze point
	Coco PEG DHP (flex)		50	Gel formed during addition
	Coco Glyceryl (non-gemini)		775	Gel formed during addition
	Castor HP (rigid) Castor PEG DHP (flex)		35	No gel formed, no haze point
		91.3	75	Gel formed during addition
,	Castor Glyceryl (non-gemini) Coco/Castor PEG DHP (flex)	Soluble to a 1:1 ratio	64	No gel formed, no haze point

provided foam. Regardless of the alkyl group, the foam height followed the following order:

Glyceryl < Flexible < Rigid

Wetting Results

The Draves wetting times were quite different for SLS and SLES-2 (see **Figure 11**, on page 66). The coco-glyceryl quat had the longest wetting time by far in SLS, and the coco flexible quat had the longest wetting time in SLES-2.

General Conclusions

The surfactant properties of anionic and cationic materials are determined by interactions between the two. The complex that forms determines not only solubility in water, but also how the complex packs at the surface and ultimately the surfactant properties. Optimization of properties vis-à-vis foam, detergency, wetting and irritation likely will be an area of much activity in personal care as work is conducted to provide optimum performance in complex formulations.

Surfactant Literature References

A literature review provides insight into the recent interest in gemini surfactants. While the basic concept has been known for quite some time, it was in the

1990s that the interest grew in these surfactants. Recent pioneer work has been performed by a group of researchers, including: Milton Rosen, David Tracy, Ruoxin Li, Manilal Dahanayake and Jiang Yang. This area of surfactant research will almost certainly enjoy

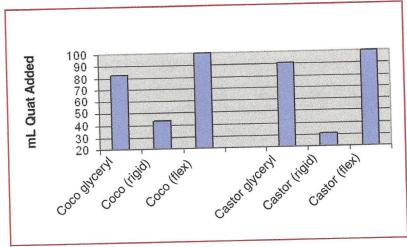


Figure 7. Quat interaction with SLS

increased usage. Important reference information about gemini surfactants can be found in the following references:

- 1. U.S. Patent Number 2,374,354, issued in 1945—Describes gemini surfactants used for flotation and emulsification.
- 2. U.S. Patent Number 2,524,218 and 2,530,147, issued in 1950—Describes surfactants with two hydrophobic tails and three hydrophilic heads that are claimed to give good detergency and wetting properties.
- 3. U.S. Patent Number 3,244,724, issued in 1966-Sulfoalkylated Imidazolines; describes a class of compounds that are anionic detergent compatible and, at the same time, softeners.
- 4. U.S. Patent Number 3,888,797, issued in 1975 and related patent U.S. Patent 3,855,156, 1974—Discloses a number of nonionic gemini surfactant species in which the hydrophobic portion is comprised of a long-chain lower alkyl or alkylene while the hydrophilic
- portion is comprised of an ethoxylate group. These materials are said to be outstanding detergents that give soil resistance to fabrics.
- 5. U.S. Patent Number 4,892,806 (Briggs) and EP 0,688,781, A1 (Adams)-Discloses sugar-based hydrophilic heads joined to the hydrophobic counterpart by a short-chain carbon bridge. Each moiety would contain a hydrophilic group, e.g., polyoxyethylene, and a hydrophobic group, e.g., an alkyl chain.
- 6. U.S. Patent 5,160,450, issued in 1992—While not using the term gemini surfactants, discloses a class of compounds that have the necessary spacer units and the fatty tails. The invention describes surface-active agents, having two hydrophobic chains and two hydrophilic groups exhibiting properties suitable as emulsifiers, detergents, dispersants and solubilizing agents for use in the fields of industrial, cosmetic, domestic and medical goods.
- 7. U.S. Patent Number 5,534,197, issued in 1996—Describes gemini polyhydroxy fatty acid amides; describes gemini polyhydroxy fatty acid amide compounds and laundry, cleaning, fabric and personal care compositions

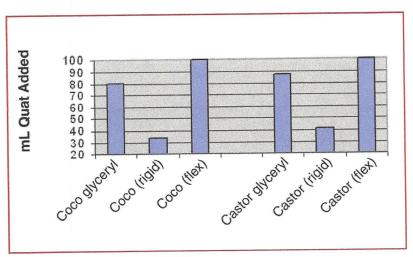


Figure 8. Quat interactions with SLES-2

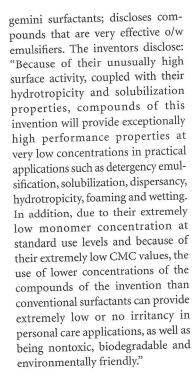
SLES -2	Quat sample	Grams added to haze point	Viscosity @ 21.5°C	Notes
1	Coco HP (rigid)	33.7	230	Gel formed during addition
2	Coco PEG DHP (flex)	Soluble to a 1:1 ratio	332.5	Gel formed during addition, no haze
3	Coco Glyceryl (non-gemini)	80.1	135	Gel formed during addition
4	Castor HP (rigid)	41.4	210	Gel formed during addition
5	Castor PEG DHP (flex)	Soluble to a 1:1 ratio	57	No gel formed, no haze point
6	Castor Glyceryl (non-gemini)	87.5	95	No gel formed during addition
7	Coco/Castor PEG DHP (flex)	Soluble to a 1:1 ratio	180	No gel formed, no haze point

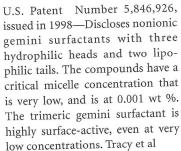
Product	Immediate (mm)	1 min (mm)	5 min (mm)	Draves (sec)
Coco HP (rigid)	170	150	140	8.0
Coco PEG DHP (flex)	165	145	135	9.0
Coco Glyceryl (non-gemini)	15	13	13	66.5
Castor HP (rigid)	170	150	140	6.5
Castor PEG DHP (flex)	150	140	130	5.8
Castor Glyceryl (non-gemini)	155	130	125	4.4
Coco/Castor PEG DHP (flex)	165	145	140	3.97

comprising these compounds, and teaches a method for the preparation of a nonionic gemini surfactant wherein the hydrophilic head is a sugar or carbohydrate while the hydrophobic head is a long-chain alkyl, the two joined by a short alkyl chain.

- 8. U.S. Patent Number 5,585,516, issued in 1996—Describes two tail-two head and two tail-one head surfactants;
- discloses two tail-two head and two tail-one head surfactants including biphenolic hydrocarbon moieties.
- A series of patents covering gemini surfactants assigned to Rhodia is important to this class of materials. These include:

U.S. Patent Number 5,811,384, issued in 1998—Disclosed nonionic





U.S. Patent Number 5,863,886, issued in 1999—Discloses nonionic gemini surfactants having multiple hydrophobic and hydrophilic sugar groups; discloses: "The molecular structure provides energetically favorable decreases in the free energy of adsorption and micellization through the favorable distortion

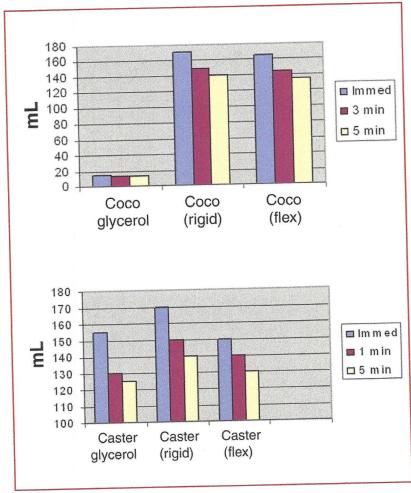


Figure 9. SLS quat combination foam

Product	Immediate (mm)	1 min (mm)	5 min (mm)	Draves (sec)
	165	145	140	11.7
Coco HP (rigid)	155	140	130	16.3
Coco PEG DHP (flex)		10	7	8.6
Coco Glyceryl (non-gemini)	No initial foam		150	6.0
Castor HP (rigid)	175	155		9.0
Castor PEG DHP (flex)	150	140	135	
Castor Glyceryl (non-gemini)	150	130	130	3.4
Coco/Castor PEG DHP (flex)	160	140	135	5.3

of water structure, and at the same time providing a close-packed arrangement at the interface. This is reflected by the relatively low surface area per molecule that is unexpected from the molecular dimensions for the molecule. The area per molecule for the compounds of the invention is comparable to corresponding conventional surfactants. The ability of the compounds of the invention to distort water structure through inhibition of crystalline or liquid crystalline phase formation in bulk phase and at the same time to pack closely on adsorption at the interface is contrary to conventional wisdom."

This again demonstrates the uniqueness of the molecular design for these compounds, which is critical to providing the unexpected exceptional surface and performance properties. The exceptional surface activity and unique structural features of the surfactants of the present invention provide two other important performance properties that can have immense practical application in industry. One is their hydrotropicity, which is the ability of organic substances to increase the solubility of other insoluble organic substances in water. Secondly is their solubilization, or the ability to dissolve water-insoluble organic compounds into aqueous surfactant solutions above their CMC levels. The compounds of the invention, because of their very low CMC values, are efficient solubilizers. This latter property will not only allow the formulation of homogeneous water-insoluble materials, but also will enhance the surface activity of other surfactants whose low water solubility restricts their use. These novel surfactants of the invention are far better than comparable conventional surfactants in hydrotroping and solubilizing properties.

Regardless of the alkyl group, the foam height followed the following order:

Glyceryl < Flexible < Rigid

Because of their unusually high surface activity, coupled with their hydrotropicity and solubilization properties, compounds of this invention will provide exceptionally high performance properties at very low concentrations in practical applications such as detergency emulsification, solubilization, dispersancy, hydrotropicity, foaming and wetting. In addition, due to their extremely low monomer concentration at standard use levels, and because of their very low CMC values, the use of lower concentrations of the compounds than conventional surfactants can provide extremely low or no irritancy in personal care applications, as well as being nontoxic, biodegradable and environmentally friendly.

U.S. Patent Number 5,900,397, issued in 1999—Discloses nonylphenol nonionic gemini surfactants; discloses: "Novel nonylphenol nonionic gemini surfactants are extremely effective emulsifiers for o/w emulsions that provide improved detergency at even low concentration levels."

U.S. Patent Number 5,922,663, issued in 1999—Discloses an enhancement of soil release with gemini surfactants; discloses a composition comprising a conventional surfactant, a gemini surfactant and a polymeric soil release agent. The compositions are useful as surfactant additive packages, detergents and fabric softeners.

U.S. Patent Number 5,945,393, issued in 1999—Discloses nonionic

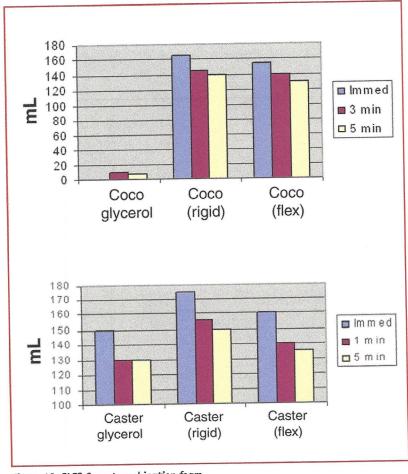


Figure 10. SLES-2 quat combination foam

gemini surfactants; discloses: "Novel nonionic gemini surfactants are extremely effective emulsifiers for o/w emulsions that provide improved detergency at even low concentration levels."

U.S. Patent Number 5,952,290, issued in 1999—Discloses anionic gemini surfactants and methods for their preparation; discloses: "a new, and improved class of anionic gemini surfactants consisting of two hydrophilic groups and two hydrophobic moieties joined by a bridge that possess improved surfactant functionalities yet may be characterized as mild for use in personal care products and environmentally benign."

U.S. Patent Number 6,204,297, issued in 2001—Discloses nonionic gemini surfactants; discloses: "Novel nonionic gemini surfactants are extremely effective emulsifiers for o/w emulsions that provide improved detergency at even low concentration levels."

10. U.S. Patent Number 6,034,271, issued in 2000-Discloses betaine gemini surfactants made from amines; discloses: "products that are characterized, in comparison with their conventional equivalents, by significantly lower critical micelle formation concentrations, as well as significantly lower surface tensions of the aqueous solutions of the surfactants according to the invention, as well as significantly lower surface tensions between the said aqueous solutions and various oils, such as paraffin oil, but also thyme oil or various triglycerides. Furthermore, the surfactants, according to the invention, demonstrate extraordinary mildness and gentleness to the skin."

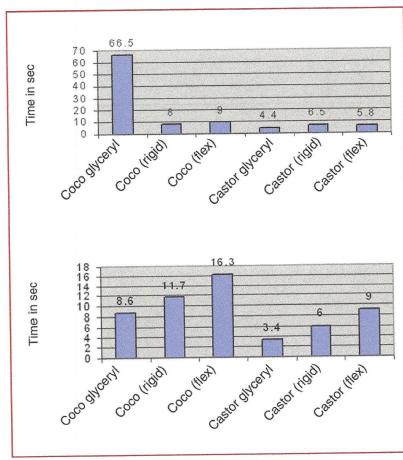


Figure 11. SLS and SLES-2 quat combination Draves time

11. A number of Cognis' recent patents have issued that include:

U.S. Patent Number 6,666,217, issued in 2003—Describes gemini surfactants in cleaning compositions; discloses: "Gemini surfactants, optionally in combination with ingredients customary in rinse aids, optionally with further nonionic surfactants and anionic surfactants, and to the use of the gemini surfactants for improving the wetting behavior in rinse aids."

U.S. Patent Number 6,777,384, issued in 2004—Discloses: "Gemini surfactants, optionally in combination with ingredients customary in laundry detergents, dishwashing detergents and cleaners, optionally with further nonionic surfactants and anionic surfactants, and to the use of such gemini surfactants for improving the wetting behavior and the compatibility with plastics, for the simplified preparation of solid cleaners and as foam-suppressing surfactant in rinse aid formulations."

U.S. Patent Number 6,794,345, issued in 2004—Discloses: "Gemini surfactants, optionally in combination with ingredients customary in dishwashing detergents and cleaners, optionally with further nonionic surfactants and anionic surfactants, and to the use of such gemini surfactants for improving the wetting behavior and the compatibility with plastics, for the simplified preparation of solid cleaners and as foamsuppressing surfactant in rinse aid formulations."

U.S. Patent Number 6,797,687, issued in 2004—Discloses: Gemini surfactants are "useful as components in laundry detergents, dishwashing detergents and cleaners, and for improving the wetting behavior on various surfaces."

U.S. Patent Number 6,805,141, issued in 2004—Discloses mixtures of gemini surfactants and fatty alcohol alkoxylates in rinse agents.

U.S. Patent Number 6,982,078, issued in 2006-Discloses a novel class of polymeric gemini compounds having specific quaternized amine based upon a dimer acid amido amine quaternary compound. The materials are substantive to human skin and are well-tolerated by human tissue, making them suitable for use preparation of barrier products for personal care applications.

Gemini Surfactant Literature References

A number of gemini surfactants are reported in the literature:

1. Zhu et al, J of the Amer Oil Chem Soc (JAOCS) 68 7,539—Teaches the preparation and properties of bis(sulfonate) amphipathic compounds with three long-chain alkyl groups. The compounds were prepared by reacting n-acetyldiethanolamine diglycidylethers with long-chain fatty alcohols. These triple-chain surfactants are asserted to be soluble in water and exhibit superior micelle formation and surface active properties than conventional single-chain surfactants. (1991)

- 2. Zhu et al, JAOCS 69 7,626-Discloses the preparation and properties of glycerol-derived double or triple-chain surfactants with two hydrophilic ionic groups. The ionic groups are comprised of sulfate, sulfonate and carboxylate groups, and the surfactants allegedly exhibit superior surface active properties such as micelle formation and the ability to lower surface tension as opposed to conventional single- and even double-chain surfactants. (1992)
- 3. Gao et al. JAOCS 71 7,771-Investigates the dynamic surface tensions of a number of surfactants, some being gemini surfactants with three hydrophobic chains. It is asserted that the apparent diffusion coefficient decreases with an increase in the number of alkyl chains and the resulting bulkiness of the surfactant molecule. (1994)

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Send e-mail to author Tony O'Lenick at tolenick@mindspring.com.

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