

# Effect of Selected Non-Ionic Surfactants on the Flow Behavior of Aqueous Veegum Suspensions

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## ABSTRACT

The aim of this work was to investigate the influence of some non-ionic surfactants, Tween 80 and Brij 98, on the viscosity and flow behavior of a commercial montmorillonite clay, Veegum Granules. The effect of different concentrations of the surfactants on the shear stress–shear rate rheograms of hydrated concentrated clay suspensions was determined by shear viscometry. The addition of either surfactant increased the plastic viscosity and the yield stress of the suspensions. Furthermore, both surfactants altered the thixotropy of the suspensions to an extent that depended on both the surfactant concentration and the time of equilibration of the surfactant and Veegum. Brij 98 had a greater and more rapid effect. It is proposed that the surfactant polar head-groups anchor at the tetrahedral sheet surface, leaving the alkyl chains extending away from the edges and faces. Consequently, the alkyl chains undergo hydrophobic interactions that facilitate the association between the platelets and increase the physical structure within the suspension. Stereochemical differences between the polar groups may lead to differences in the way the surfactants associate with the tetrahedral sheet and hence their ultimate effect on the rheological behavior. There is a significant interaction between these surfactants and montmorillonite clays, and the rheological changes that occur could have a major impact on any pharmaceutical formulation that uses these ingredients.

**KEYWORDS:** Montmorillonite clay, nonionic surfactants, rheology, thixotropy.

## INTRODUCTION

Montmorillonite is a hydrophilic expanding smectite clay with a 2:1 layer structure. This means that the primary particles (or platelets) are composed of 1 sheet containing aluminum atoms octahedrally coordinated with 6 oxygen atoms or hydroxyl groups, sandwiched between 2 sheets of silicon tetra-

hedrally coordinated to 4 oxygen atoms or hydroxyl groups.<sup>1</sup> The sheets share both oxygen atoms and hydroxyl groups. In the tetrahedral sheets there is some isomorphous substitution of aluminum for silicon, and in the octahedral sheet there is substantial substitution of magnesium and iron for aluminum. The thin, flat, approximately hexagonal platelets have a large aspect ratio. It has been estimated that the isoelectric point of the edges is  $\sim 7$ ,<sup>2</sup> and at slightly less than neutral pH, the edges bear a positive charge, while the faces are negative. The net charge on the platelets is negative, and this is balanced by exchangeable cations, predominantly sodium.

When montmorillonite clays are dispersed in water, there is an immediate increase in viscosity followed by a slower increase over many days. During this time, water that is imbibed between the clay platelets causes the macroscopic particles to swell and the platelets to exfoliate and delaminate. Although the contribution of the edge area to the total area is small (1% is a commonly used estimate<sup>3</sup>), the edge-to-face attraction is the most significant contributor to the overall association between platelets.<sup>2</sup> The platelets associate, forming the so-called house of cards structure, because of the edge-to-face contacts, and this leads to the viscosity, yield stress, and thixotropy exhibited by montmorillonite suspensions.

Abend and Lagaly<sup>4</sup> have shown that montmorillonite suspensions with a solid content of greater than 3% wt/wt display a substantial yield stress as well as thixotropic and viscoelastic flow behavior. These suspensions behave as gels. Duran et al<sup>2</sup> observed that at  $\text{pH} < 10$ , montmorillonite suspensions showed non-Newtonian behavior, and using shear rheometry, determined that a Bingham plastic model was appropriate. In this model, systems display a constant Bingham plastic viscosity and a Bingham yield stress. The yield stresses decreased from 3 to 1.3 Pa over the pH range of 6 to 9, and this reflected a loss of the house of cards structure.

Both nature and industry exploit the expanding nature of the clays, and it has been shown that they can sequester diverse and biologically significant molecules. For example, montmorillonite clay particles in both aquatic and soil media are responsible for sequestering many organic pollutants.<sup>5,6</sup> The montmorillonite clays are also widely used in many industrial and pharmaceutical applications. For example, suspensions are used as lubricating fluids in oil drilling,<sup>7</sup> and the use of the clays in pharmaceutical systems has also been reviewed.<sup>8</sup> A growing application of the clays is the development of

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nanocomposite materials. In these systems a deliberate attempt is made to intercalate a molecule (often a polymer) between the platelets of the clay. The application of such nanocomposites is diverse, ranging from coating<sup>9</sup> to pharmaceutical drug delivery systems.<sup>10,11</sup>

Several studies have investigated the effect of intercalation of ionic surfactants on the flow behavior of montmorillonite clays. The large surface area of the platelet faces, and their negative charge, may favor the aggregation of cationic surfactant molecules as hemimicelles and micelles. Recently, the interaction of cetyltrimethylammonium bromide (CTAB) with model surfaces such as silica, titanium dioxide, and mica has been probed using several techniques, including atomic force microscopy,<sup>12,13</sup> attenuated total reflectance Fourier transform infrared (spectroscopy),<sup>14,15</sup> and optical reflectometry.<sup>13</sup> Furthermore, some studies have looked at the coadsorption of both anionic and cationic surfactants. Li and Tripp<sup>14</sup> showed that mixed micelles of sodium dodecyl sulfate and CTAB form on titanium dioxide.

There has been less interest in the influence of non-ionic surfactants on montmorillonite clays. This is despite the fact that it is highly probable that such surfactants and clays could be combined in pharmaceutical formulations. The aim of this article is to investigate the influence of 2 related non-ionic surfactants, Tween 80 and Brij 98, on the viscometric behavior of a commercially available form of montmorillonite clay commonly used in pharmaceutical systems, Veegum Granules. Theoretically, both surfactants have ~20 mol of polyoxyethylene oxide (POE) per molecule: the Tween 80 has 4 short POE chains linked to the oleyl group through polyhydric sorbitan, while the Brij 98 has a single long POE chain. The work has relevance in the formulation of products containing the montmorillonite clay and non-ionic surfactants and also allows the effect of surfactant architecture to be elaborated.

## MATERIALS AND METHODS

### Materials

Veegum Granules (International Nomenclature of Cosmetic Ingredients [INCI] name: aluminum magnesium silicate, hereinafter called Veegum) were donated by the Australian agent of RT Vanderbilt Co (Norwalk, CT). Tween 80 (INCI name: polysorbate 80) and Brij 98 (INCI name: oleyl 20) were purchased from Sigma Chemical Co (St. Louis, MO). The surfactants and Veegum were used as received. Water was subjected to reverse osmosis.

### Experimental Methods

#### Suspension Preparation

A stock suspension (7.2% wt/wt) was prepared by dispersing the required weight of Veegum powder (over a period

of ~10 minutes) in 5 fractions into ~60% of the required amount of water in a high-speed blender (Braun, Frankfurt, Germany). After all the powder was incorporated, the balance of the water was added and was used to wash down any splashes off the walls of the blender vessel. The concentrated suspension was then subjected to further agitation in the blender for 2 minutes prior to being poured into a glass stock vessel.

#### Hydration and Equilibration

When wet with water, the Veegum powder imbibes water and hydrates. Some of the concentrated suspension was subject to viscosity measurement immediately, and the balance was divided into 100-mL sealed containers and stored in a refrigerator at 8°C for up to 96 hours. At specific time intervals after that, a container was removed from the refrigerator, allowed to equilibrate for 3 hours at 25°C, and immediately subjected to viscosity measurement at 25°C. Based on the changes in the plastic viscosity and the yield stress, the time interval of 3 days was chosen as the hydration time for all further experiments.

Fresh concentrated suspensions (7.2% wt/wt) were allowed to hydrate for 3 days at 8°C and then equilibrated undisturbed for 3 hours at 25°C, before samples containing a specified amount of the concentrated suspension were diluted by the addition of various weights of a stock solution of either Tween 80 or Brij 98 and water. This resulted in final suspensions that contained 6.8% wt/wt Veegum and 0% to 0.5% wt/wt surfactant. Some of these were subjected to immediate viscosity measurement at 25°C, and the remainder was stored at 25°C for periods up to 21 days. During these periods, the viscosity was measured (at 25°C) at different times.

#### Viscosity Measurement and Assessment of Flow Behavior

Duplicate samples were loaded into a cone and plate viscometer (Bohlin V88, Cirencester, UK), the gap (150 μm) was closed slowly, and the samples were sheared at 12 sec<sup>-1</sup> for 20 seconds. Then the rotation of the cone was paused for 40 seconds. This allowed the sample to gently spread uniformly in the gap and to reach thermal equilibrium with the plate that was maintained at 25°C by a water bath. Under software control, the shear rate was increased in 15 logarithmically distributed steps from 12 sec<sup>-1</sup> to 600 sec<sup>-1</sup> and then decreased back to 12 sec<sup>-1</sup> using the same 15 steps. This procedure enabled the generation of ascending and descending rheograms (shear stress vs shear rate) and viscosity plots (viscosity vs shear rate). The yield stress and plastic viscosity were determined by linear regression of the descending rheograms.

The thixotropic index (TI) is the area between the ascending and descending rheograms expressed as a percentage of the area under the ascending rheograms. A high TI suggests that the application of progressively increasing shear stresses has caused a substantial breakdown of structure within the suspension.

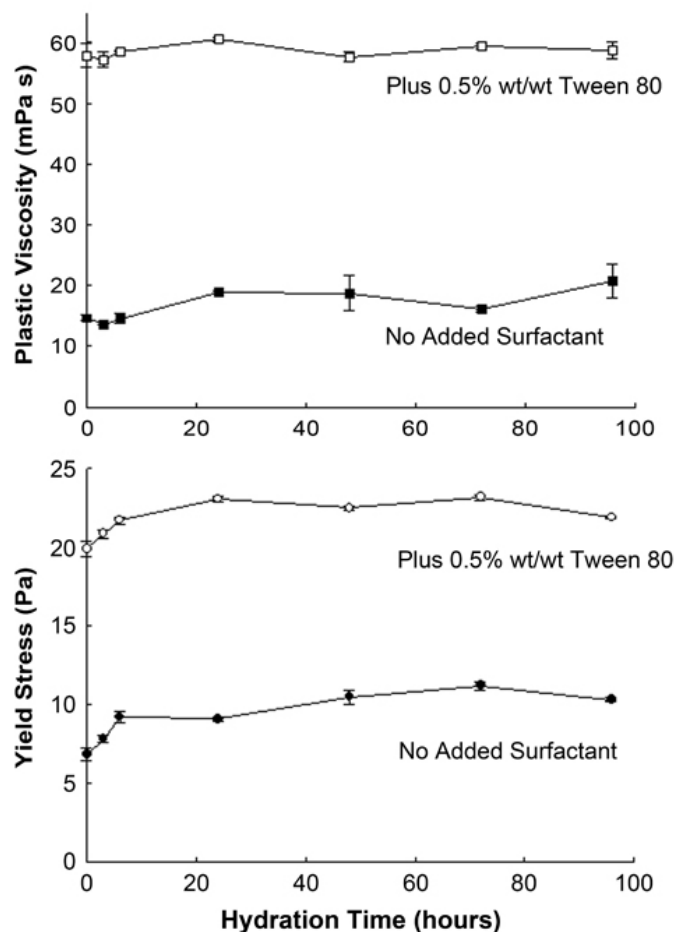
### Statistical Analysis

All results are shown as the mean of duplicates, with the error bars denoting the range of the experimental results. The data were analyzed using 1 between-subjects and 1 within-subjects variable repeated measures analysis of variance, as described by Montgomery.<sup>16</sup> The level of significance was set at  $P < .05$ , and the analysis was implemented in Microsoft Excel using a validated method.<sup>5</sup>

## RESULTS AND DISCUSSION

The development of structure within a suspension was assessed by the changes in the Bingham plastic viscosity and the Bingham yield stress. As shown in Figure 1, the plastic viscosity of a stock (7.2% wt/wt) suspension was ~18 mPa s and was largely independent of the hydration time. Although the addition of 0.5% wt/wt Tween 80 to the suspension during the hydration time more than tripled the average plastic viscosity to almost 60 mPa s, it did not alter the rate at which the ultimate value of the plastic viscosity was attained. Figure 1 also shows the effect of hydration time on the yield stress. In the suspensions (both with and without added 0.5% wt/wt Tween 80) there was a rapid increase in the yield stress during the first 6 hours of hydration. During the 90 hours that followed, the yield stress was largely unaffected. Although these results suggest that hydration occurs within ~24 hours of adding water to the powder, in the subsequent experiments a hydration time of 72 hours was allowed. This gave a high certainty that hydration equilibrium had been reached and was also logistically suitable.

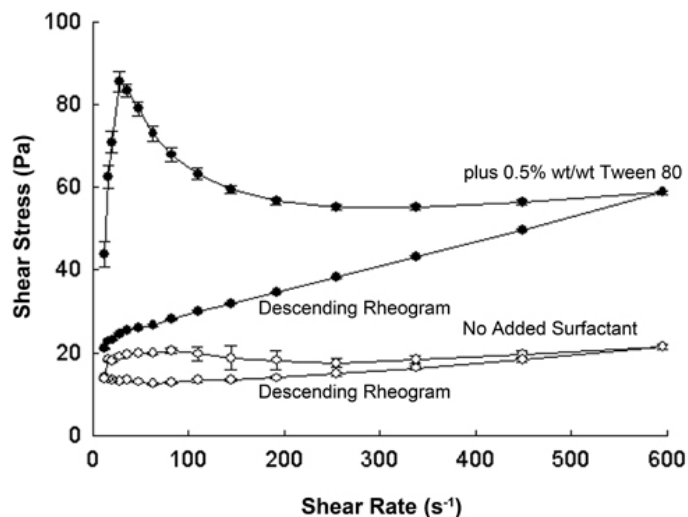
The addition of 0.5% wt/wt Tween 80 in the previous experiment was performed as a pilot study. It was clear that the added surfactant significantly increased both the yield stress and the plastic viscosity of the suspension, as shown in Figure 1. The added surfactant also changed the rheograms of the suspensions. Figure 2 shows that after hydration for 72 hours, the rheogram of the suspension without added surfactant showed minimal thixotropy; the TI was 15.8%. However, the addition of 0.5% wt/wt Tween 80 during hydration increased the TI to 30.6%. In Figures 1 and 2, it must be recognized that the suspension with added Tween 80 actually had a slightly lower concentration (6.8% wt/wt) than the suspension with no Tween 80. This is because, in this preliminary experiment, a small weight of a concentrated aqueous solution of Tween 80 was added to the 7.2% wt/wt



**Figure 1.** The effect of hydration time of a 7.2% wt/wt Veegum suspension at 8°C, with and without Tween 80, on the development of plastic viscosity and yield stress. Measurements performed at 25°C;  $n = 2$ .

Veegum before the 3-day hydration period. Figure 2 also shows that there is a very obvious spur (ie, a peak shear stress at low shear rate) in the ascending rheogram of the suspension with added surfactant. This feature will be discussed later.

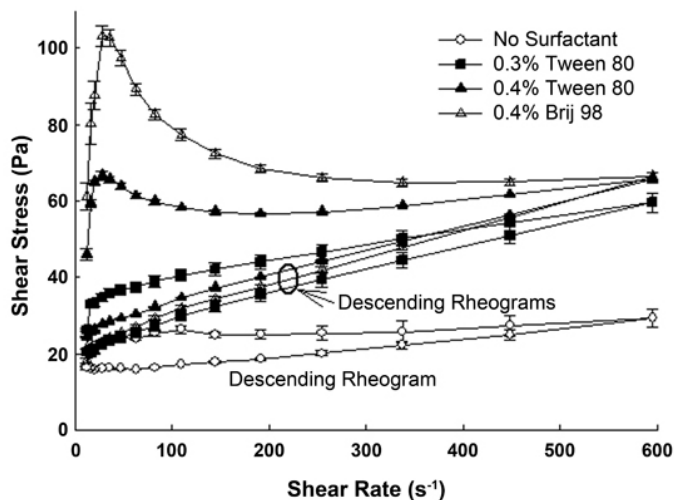
Based on the observations reported in Figure 1 and Figure 2, Veegum suspensions (7.2% wt/wt) were hydrated for 3 days and then a range of weights of a stock solution of either Tween 80 or Brij 98 in water (or water alone) were added. This resulted in Veegum suspensions (6.8% wt/wt) with 0% to 0.5% wt/wt surfactant, which were equilibrated at 25°C for periods up to 21 days. At different times after equilibration commenced, the viscosity measurements described above were made. No individual sample of suspension was subject to viscosity measurement more than once. No attempt was made to alter the pH because our aim was to assess the effect of the surfactants at the natural pH. The pH of a 6.8% wt/wt suspension of Veegum in water was measured as 9.06 at 25°C, which is above the isoelectric point of montmorillonite. Although the edge-to-face associations are dominant



**Figure 2.** The effect of Tween 80 on the steady-state shear rheograms of 6.8% wt/wt Veegum suspensions. Measurements performed at 25°C; n = 2.

at pH < 7, it has been proposed that at a pH around 9 the edge-to-edge, edge-to-face, and face-to-face associations are all similarly effective as contributors to the total energy of interaction.<sup>2</sup>

As shown in Figure 3, both surfactants caused rheological changes to the Veegum suspensions after equilibration for 3 days. Above 0.3% wt/wt of both surfactants, the ascending rheograms showed a distinct spur, that is, a peak in shear stress at low shear rates. These spurs, in part, lead to the increases in the TI of these systems. Figure 4 shows the influence of equilibration time on the rheograms of the suspensions with 0.5% wt/wt of Tween 80 or Brij 98 added. Inspection of both these figures leads to several conclusions. Increasing the concentration of either surfactant or increasing the equil-

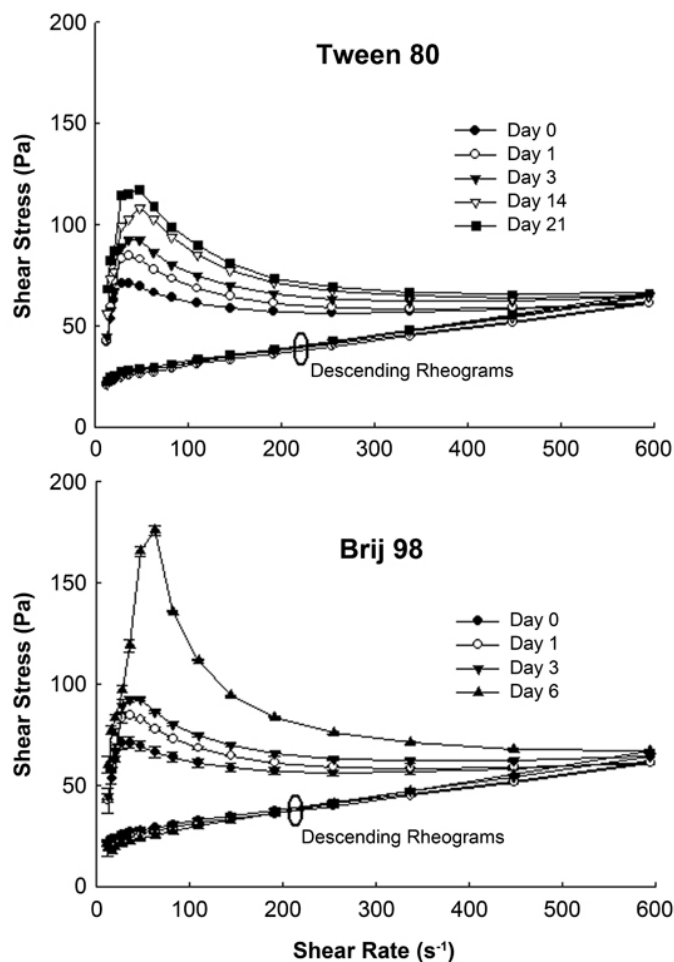


**Figure 3.** The effect of Tween 80 or Brij 98 on the steady-state shear rheograms of 6.8% wt/wt Veegum suspensions. Measurements performed at 25°C; n = 2.

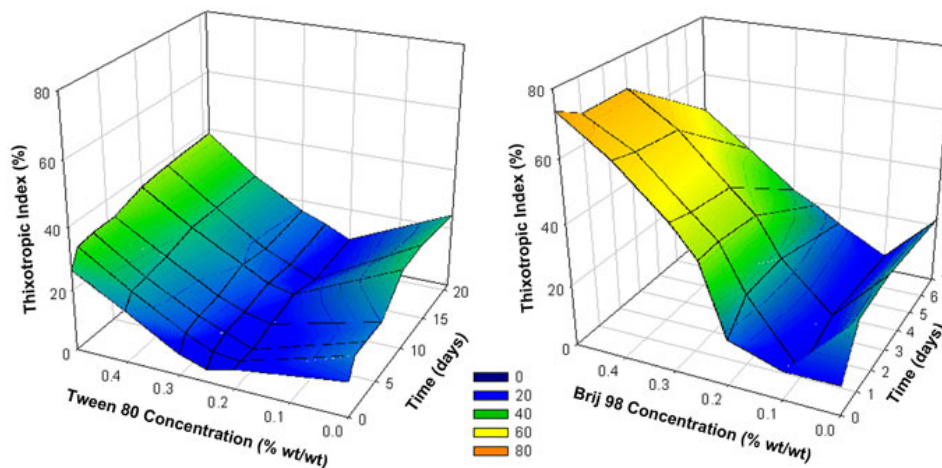
ibration time caused an increase in the peak shear stress. Additionally, the Brij 98 had a greater effect on both the peak shear stress and the rate at which the spur developed.

Similar spurs have been reported previously in suspension systems.<sup>4,9,17,18</sup> Although neither a specific explanation of their existence nor a definite mathematical method to analyze their influence has been proposed,<sup>19</sup> the spurs have generally been attributed to the breakdown of structure within the systems. It has been shown that a spur developed when montmorillonite suspensions underwent a sol-gel transition because of the addition of sodium chloride.<sup>4</sup> It is proposed that the structure that is lost is not rapidly recovered, because when a Veegum suspension was subjected to 2 consecutive ascending/descending shear rate ramps with no delay in between, the second ascending/descending ramp did not show the spur (data not shown). Burgentzle et al<sup>9</sup> reported a similar observation.

As shown in Figure 5, both surfactants caused significant changes to the TI of Veegum. Over 21 days, the TI of Veegum



**Figure 4.** The effect of Tween 80 or Brij 98 and equilibration time on the steady-state shear rheograms of 6.8% wt/wt Veegum suspensions. Measurements performed at 25°C; n = 2.



**Figure 5.** The effect of equilibration time and concentration of Tween 80 or Brij 98 on the thixotropic index of 6.8% wt/wt Veegum suspensions. Measurements performed at 25°C; n = 2.

was generally increased by any addition of Tween 80. Although additions of up to 0.25% wt/wt Tween 80 caused a decrease in the TI, higher levels caused significant increases in the TI. However, Brij 98 caused more rapid rheological changes to Veegum than Tween 80, and very substantial changes in the TI were apparent within only 7 days. In fact, after 7 days the suspensions became very paste-like, which made viscosity measurement impossible. Similarly, the TI decreased with time when the Brij 98 concentration was less than 0.2% wt/wt but increased greatly when the concentration of Brij 98 was raised above 0.2% wt/wt.

Based on the descending rheograms, estimates of the yield stress and plastic viscosity were obtained from results such as those in Figure 3. As the concentration of the surfactants was increased from 0% to 0.3% wt/wt, there was a marked increase in the Bingham plastic viscosity (up to 70–80 mPa s), and the yield stress was increased up to 19 to 26 Pa. For both parameters, Brij 98 had a greater effect on Veegum.

The polar head-groups of the surfactants would be expected to strongly adsorb onto both the faces and the edges of the platelets.<sup>20</sup> They showed that POE chains in oleth-type surfactants adsorbed to smectite surfaces through hydrogen bonding between oxygen atoms in the POE chain and water molecules in the hydration layers of exchangeable cations such as calcium and magnesium, and ion-dipole interactions between the POE oxygens and the cations. Furthermore, it was proposed that the POE chain would assume an extended helical conformation that would maximize exposure of the oxygen atoms to both the water molecules and the cations.<sup>20</sup> Based on the interlayer spacing (determined by their X-ray diffraction data), Deng et al<sup>20</sup> concluded that no more than 2 layers of POE chains intercalated between the clay platelets. Intercalation of the surfactants between the platelets in the current study would assist the further delamination of undissociated platelets and increase the number of potential

contact points between platelets. The increases in TI, and the development of the spurs at surfactant concentrations above 0.3% wt/wt (Figures 3 and 4), suggest that both Tween 80 and Brij 98 interact with Veegum, and it is likely that there is a hydrophobic association between the alkyl chains that results in increased association between the clay platelets.

In addition, data (based on X-ray diffraction and molecular modeling) on the intercalation and self-association of polar n-alkyl pyrrolidones on montmorillonite<sup>21</sup> showed that (1) the polar domain of the molecules interacted with exchangeable surface cations of the clay by an ion-dipole mechanism, (2) the pyrrolidone group lay parallel to the tetrahedral sheet, (3) the alkyl chain, if greater than 8 carbons long, extended (pillar-like) away from the tetrahedral sheet at  $\sim 90^\circ$ , and (4) 18 to 22 carbon alkyl chains are necessary to obtain stable complexes. Beall and Goss<sup>21</sup> also showed that for a series of n-alkyl alcohols, the molecules lay flat on the tetrahedral sheet when the carbon chain was less than 10 atoms long but that longer alkanol chains also formed a self-associated structure at  $90^\circ$  to the surface.

It appears likely that differences in the molecular architecture of the 2 surfactants alter the way they interact with the Si-O-Si surfaces and, in consequence, the way they affect the flow behavior of the Veegum suspension. The single POE chain in Brij 98 may provide greater anchorage of Brij 98 to the surface relative to Tween 80, in which the polar group is composed of 4 short POE chains (each nominally comprising 5 ethylene oxide units) radiating from a sorbitan molecule. Another issue that could influence the apparent difference between the performance of the 2 surfactants is that POE-based non-ionic surfactants are known to show heterogeneous composition.<sup>22,23</sup> These results could be critical in the formulation of topical products that include both Veegum and surfactant. For example, montmorillonite clays may be used as an additive in semisolid topical sunscreens. Based on these

results, the inclusion of Brij 98 or Tween 80 would be expected to increase the thixotropy of the system, and thixotropic behavior in sunscreens has the potential to lead to poor in vivo performance.<sup>24</sup>

## CONCLUSIONS

The results show there is an interaction between the non-ionic surfactants, Tween 80 and Brij 98, and the montmorillonite clay Veegum that leads to a large increase in the plastic viscosity, yield stress, and thixotropy of the clay-surfactant suspensions. The Brij 98 acts more strongly and rapidly than the Tween 80, which may be due to differences in the architecture of the polar domains. This interaction could be critical in any formulation that combined the clay and the surfactant, and further work is in progress to attempt to elucidate the physicochemical nature of the interaction.

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