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## Effect of Adsorbed Surfactants on the Rheology of Colloidal Zirconia Suspensions

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The effect of cationic and anionic surfactant additives on the shear yield stress ( $\tau_y$ ) and electrokinetic behavior of concentrated zirconia ( $\text{ZrO}_2$ ) suspensions has been investigated. The two pairs of surfactants studied were dodecylamine hydrochloride (DAC) and dodecyltrimethylammonium chloride (DTAC) and sodium dodecyl sulfate (SDS) and sodium dodecylbenzyl sulfate (SDBS). Each of the pairs differs only in the chemical structure of its headgroup. Adding each of the surfactants to concentrated zirconia suspensions increased the maximum yield stress for pH 3–11; however, within each pair, the magnitude of the increase varied substantially. The effect of added surfactant on zirconia electrokinetic behavior was not nearly as sensitive to headgroup chemical structure. Adsorption isotherms indicated that surfactant was present on the surface at very low coverage. Since the size of surfactant surface aggregates is known to be linked to headgroup chemical composition, the observed rheology could be related to such aggregate structures. In addition to demonstrating the sensitivity of concentrated suspension rheology to the exact chemical details of surfactant additives, these results suggest new interpretations of the role surfactant adsorption plays in determining the rheology of these mixtures.

### Introduction

The rheology of aqueous colloidal suspensions is affected by surfactant additives in ways that have been exploited in ceramic and mineral processing, coal–water slurry preparation, and pulp, paper, and ink production.<sup>1–3</sup> In colloidal systems, the rheology is determined by the combined effects of particle size, shape, and size distribution as well as by hydrodynamic interactions, Brownian motion, and interparticle forces. Forces relevant to the rheology of colloidal metal oxide particles in the aqueous phase with dissolved surfactants include interparticle attractions due to van der Waals forces and electrostatic repulsions due to diffuse double layers surrounding the charged particles. Additional interactions arising from the dissolved and adsorbed surfactants must also be considered.

Under certain conditions the nature and magnitude of interparticle forces can be deduced from the suspension rheology. The shear yield stress ( $\tau_y$ ) of coagulated/flocculated aqueous suspensions of metal oxide particles is one such instance.<sup>4,5</sup> In these systems, the effect of solution ionic strength and pH on  $\tau_y$  can be understood in

terms of interparticle van der Waals and electrostatic interactions (DLVO forces). Specifically, at the suspension isoelectric point (IEP), in the absence of specific interactions, repulsive electrostatic interactions are minimized and the suspension is in a state of maximum coagulation; the measured  $\tau_y$  is thus a maximum. As the pH of the suspension is adjusted away from the IEP, electrostatic repulsions increase (as characterized by an increasing magnitude of the  $\zeta$ -potential), and  $\tau_y$  decreases approximately as the square of the  $\zeta$ -potential.<sup>4</sup> Increasing ionic strength screens electrostatic repulsion between particles, thus ameliorating the decrease in  $\tau_y$  at a given magnitude of the  $\zeta$ -potential.<sup>6</sup> Here, the shear yield stress is defined as the minimum shear stress for which the material flows.<sup>7</sup>

In suspensions where interparticle forces are solely of electrostatic and van der Waals origin, theories are available which predict how  $\tau_y$  scales with  $\zeta$ -potential, Hamaker constant, and particle size.<sup>5,8–9</sup> The quantitative effect of particle size distribution and volume fraction has also been considered.<sup>5,9</sup> Although the role of DLVO forces in the yielding of spherical particle suspensions is well understood, the same is not true for the additional forces induced by chemical additives. Previous experimental work has demonstrated that  $\tau_y$  can be extremely sensitive to small quantities of added polyelectrolytes, small

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(1) Simon, C. In *Coagulation and Flocculation*; Dobias, B., Ed.; Surfactant Science Series Vol. 47; Marcel Dekker: New York, 1993; p 539.

(2) Botsaris, G. D.; Glazman, Y. M. In *Interfacial Phenomena in Coal Technology*; Botsaris, G. D., Glazman, Y. M., Eds.; Surfactant Science Series Vol. 32; Marcel Dekker: New York, 1989; p 199.

(3) Hunter, R. J. *Introduction to Modern Colloid Science*; Oxford University Press: Oxford, 1993.

(4) Leong, Y. K.; Boger, D. V.; Scales, P. J.; Healy, T. W.; Buscall, R. J. *J. Chem. Soc., Chem. Commun.* **1993**, 7, 639.

(5) Leong, Y. K.; Scales, P. J.; Healy, T. W.; Boger, D. V. *J. Am. Ceram. Soc.* **1995**, 78, 2209.

(6) Boger, D. V. Lecture Series 1994–03, Von Karman Institute for Fluid Mechanics, 1994.

(7) Nguyen Q. D.; Boger, D. V. *Annu. Rev. Fluid Mech.* **1992**, 24, 47.

(8) Firth, B. A.; Hunter, R. J. *J. Colloid Interface Sci.* **1976**, 57, 266.

(9) Kapur, P. C.; Scales, P. J.; Boger, D. V.; Healy, T. W. *AIChE J.* **1997**, 43, 1171.

molecule organic and inorganic adsorbates, and surfactants.<sup>10–12</sup> These studies have sought to interpret yield stress measurements in terms of additive effects on the forces between particles. Nevertheless, a satisfactory understanding of additive effects has not yet been achieved, except perhaps for small, hydrophilic molecular adsorbates.<sup>10</sup>

We focus here on the effect of surfactants on the suspension yield stress because  $\tau_y$  has been previously shown to be particularly sensitive to underlying forces and microstructure. Nevertheless, surfactant effects on other suspension rheological quantities have also been widely studied (cf., for example, refs 13–15).

Understanding the effects of surfactants on  $\tau_y$  has been hampered by incomplete knowledge of the relevant interparticle forces as well as insufficient insight into the nature of surfactant adsorption on the colloid surfaces. It is reasonable to hypothesize that the aforementioned forces and adsorption in surfactant/particulate suspensions will be sensitive to the exact chemical nature of the surfactant additive. The aim of this work is to compare the rheological, electrokinetic, and adsorption behavior of surfactants differing only in the chemical structure of their headgroups. We will show that the suspension rheology is affected to a much greater degree by such subtle chemical differences as either the electrokinetic or adsorption behavior.

This work, considered in conjunction with literature results from the surface force apparatus (SFA) and atomic force microscope (AFM), points to the possible significance of surfactant aggregate structure in determining the rheology of colloidal suspensions containing surfactant additives. Aggregate structures complicate direct interpretation of the rheology in terms of the forces between the surfactants and particles. These results further highlight the sensitivity of rheology to the exact chemical nature of surfactant additives.

## Materials and Methods

Two pairs of chemically similar surfactants were used to demonstrate the sensitivity of  $\tau_y$  to surfactant headgroup chemical structure. The first pair was dodecylamine hydrochloride (DAC) and dodecyltrimethylammonium chloride (DTAC). DTAC differs from DAC only in the degree of methyl substitution of the headgroup amine. The second pair was sodium dodecyl sulfate (SDS) and sodium dodecylbenzyl sulfate (SDBS). SDBS and SDS differ in chemical composition only by a phenyl group. Experiments were also conducted using cetyltrimethylammonium chloride (CTAC). Surfactants were obtained from Aldrich and Tokyo Kasei Kogyo and used as received. Given the amounts of surfactant found to be adsorbed on the particle surfaces (cf. Results), the equilibrium solution concentration of each species

was well below its critical micelle concentration (cmc), even for the high-electrolyte conditions of this study.<sup>16–19</sup>

The suspended particles were colloidal zirconia (ZrO<sub>2</sub>, from Z-Tech, ICI Advanced Ceramics, Australia). In addition to being an important ceramic precursor, colloidal zirconia is convenient for study because the material surface chemistry is such that the particles vary from being highly positively charged to highly negatively charged over the pH range 3–11. The particles have a BET surface area of 15.1 m<sup>2</sup> g<sup>-1</sup> and a solids density of approximately 5900 kg m<sup>-3</sup>. Their particle size distribution is characterized by  $D_{90} = 0.26 \mu\text{m}$ ,  $D_{50} = 0.21 \mu\text{m}$ , and  $D_{10} = 0.17 \mu\text{m}$  (as measured with a Leeds and Northrop Microtrac particle size analyzer). Here,  $D_{50}$  is, for example, the intensity averaged diameter for which 50% of the particles are smaller. On the basis of a conductivity measurement, the solution electrolyte concentration due to leached surface salt was 0.05 M KCl equivalent for the particle loadings of this study.

Water was from a Millipore Milli-Q water purification unit. Experiments were conducted at  $25 \pm 1^\circ\text{C}$ . A Radiometer Copenhagen PHM82 standard pH meter was used for pH measurement.

Suspensions were prepared in the following manner: For each species, a concentrated surfactant solution was first prepared. In the case of DAC, slight warming of the solution was necessary for complete dissolution. Appropriate amounts of water, zirconia, and surfactant on a dry weight percent basis (dwb%) were placed in a 50 mL container. The background electrolyte concentration was adjusted to 0.1 M potassium chloride (KCl). The sample was then sonicated for 45 s using a 0.75 in. horn and a Branson Sonifier 450. The vibrational output was 20 kHz, and the maximum power output was 400 W. The sonifier was operated between 70 and 80% of maximum power. Prepared suspensions were rested a day before measurement. Note that surfactant amounts are quantified on a dry weight basis in this study, since the equilibrium solution concentration of surfactant varies strongly with pH due to adsorption/desorption on the zirconia surfaces. The relationship between surfactant dwb% and equilibrium solution concentration will be developed subsequently from adsorption measurements.

Concentrated potassium hydroxide (1–10 M) and hydrochloric acid (1–10 M) were used to change pH. Amounts added were minimized to prevent sample dilution. Suspensions were re-dispersed by sonication if localized coagulation was observed upon addition of acid or alkaline droplets. Because long equilibration times were sometimes observed for the desorption of species from particle surfaces, pH was adjusted in a manner that promoted adsorption. The ZrO<sub>2</sub> has an isoelectric point (IEP) at pH = 7.8 (with particles being positively charged at lower pH and negatively charged at higher pH). Thus, for cationic surfactants, pH was adjusted from acid to alkaline conditions. The reverse procedure was adopted for anionic species. Long adsorption equilibration times were allowed to further reduce the possibility of nonequilibrium adsorption/desorption effects.

The static shear yield stress was measured with a vane rheometer, a technique appropriate for concentrated particulate systems. Details of vane rheometry are available elsewhere.<sup>20–22</sup> Vane measurement errors have been previously estimated to be approximately 10%.<sup>23</sup> Although the formal existence of a yield stress for fluid-like materials has been questioned, the shear yield stress as measured by the vane is well established as an indicator of interparticle forces and microstructure in mineral suspensions.<sup>10,24</sup> Yield stress measurements were conducted at zirconia loadings of 57 wt % (18 vol %). Zirconia suspensions at this concentration are, rheologically, strongly gelled over a wide range of pH, thus facilitating the vane measurement. It has been previously demonstrated that the effect of additives on metal oxide yielding rheology is not a strong function of the particle loading.<sup>12</sup> Consequently, measurements at a single particle concentration were considered sufficient for the purposes of this study.

(10) Leong, Y. K.; Scales, P. J.; Healy, T. W.; Boger, D. V. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 2473.

(11) Leong, Y. K.; Scales, P. J.; Healy, T. W.; Boger, D. V. *Colloids Surf., A* **1995**, *95*, 43.

(12) Leong, Y. K.; Boger, D. V.; Scales, P. J.; Healy, T. W. *J. Colloid Interface Sci.* **1996**, *181*, 605.

(13) Pingret, F. J. V.; Sohm, R. H.; Tadros, Th. F. *Colloids Surf.* **1992**, *65*, 85.

(14) Ducker, W. A.; Luther, E. P.; Clarke, D. R.; Lange, F. F. *J. Am. Ceram. Soc.* **1997**, *80*, 575.

(15) Fagan, M. E.; Zukoski, C. F. *J. Rheol.* **1997**, *41*, 373.

(16) Fuerstenau, D. W.; Herrera-Urbina, R. In *Cationic Surfactants, Physical Chemistry*; Somarandaran, P., Moudgil, B. M., Eds.; Surfactant Science Series Vol. 37; Marcel Dekker: New York, 1991; p 407.

(17) Mukerjee, P.; Mysels, K. J. *Critical Micelle Concentrations of Aqueous Surfactant Systems*, NSRDS-NBS 36; National Bureau of Standards: Washington, DC, 1971.

(18) Rosen, M. J. *Surfactants and Interfacial Phenomena*; Wiley: New York, 1989; Chapter 3.

(19) Gershman, J. W. *J. Phys. Chem.* **1957**, *61*, 581.

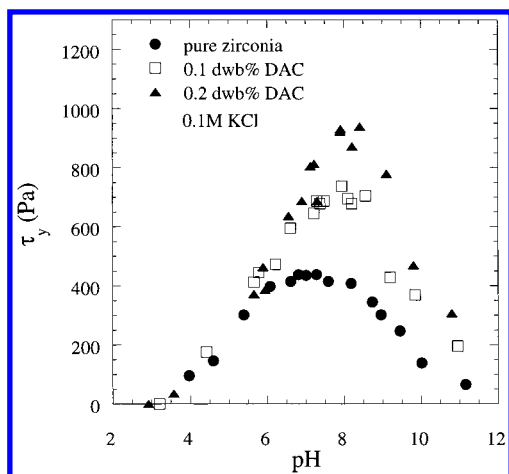
(20) Nguyen, Q. D.; Boger, D. V. *J. Rheol.* **1983**, *27*, 321.

(21) Nguyen, Q. D.; Boger, D. V. *J. Rheol.* **1985**, *29*, 335.

(22) Liddell, P. V.; Boger, D. V. *J. Non-Newtonian Fluid Mech.* **1996**, *63*, 235.

(23) Green, M. Ph.D. dissertation, Melbourne University, 1997.

(24) Barnes, H. A.; Walters, K. *Rheol. Acta* **1985**, *24*, 323.



**Figure 1.** Effect of the cationic surfactant DAC on the yield stress of 57 wt % zirconia suspensions with 0.1 M KCl.

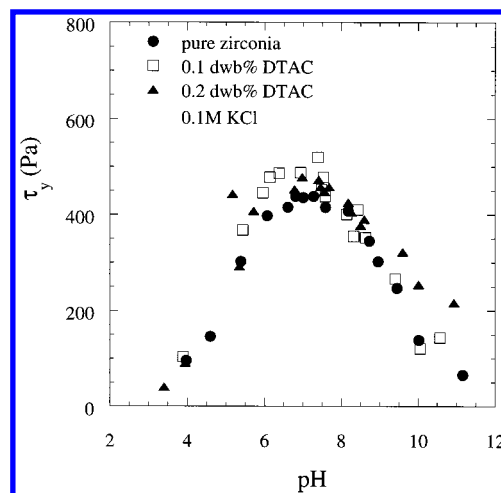
The effect of surfactant additives on aqueous  $\text{ZrO}_2$  electrokinetic properties was determined at 2 vol % with a Matec Acoustosizer. The instrument measures an electrokinetic sonic amplitude (ESA) spectrum that is converted to a frequency dependent dynamic mobility by means of the theory of O'Brien.<sup>25</sup> A  $\zeta$ -potential is further computed from the dynamic mobility by means of theories developed for dilute suspensions.<sup>26</sup> Previous work indicates that  $\zeta$ -potentials measured by the ESA technique in the volume fraction range studied are equivalent to those measured by standard electrophoretic methods.<sup>26</sup>

Adsorption isotherms for DAC and SDBS on zirconia were measured. Known quantities of surfactant were added to aqueous solutions of approximately 1 vol % zirconia. After equilibration, filtered aliquots were analyzed by absorption spectroscopy to determine surfactant concentrations. SDBS adsorption was monitored at  $\lambda = 220$  and 260 nm. DAC concentrations were determined by the chloroform extraction of its picric salt ( $\lambda = 410$  nm) according to the procedure of Iwasaki and de Bruyn.<sup>27</sup> Adsorption isotherms for SDS or DTAC were not generated.

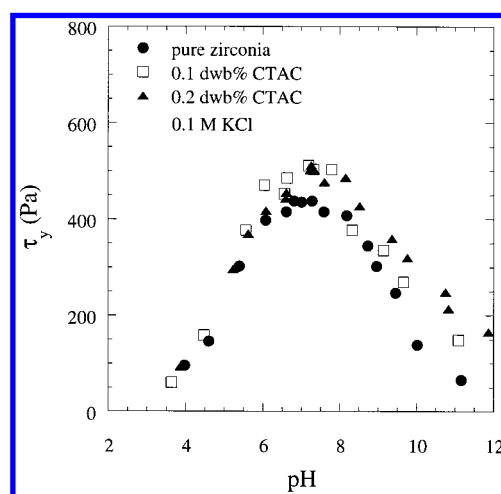
## Results

**Shear Yield Stress.** A qualitative difference between the effect of two cationic surfactants differing only in headgroup chemical composition on the yielding of concentrated zirconia suspensions is demonstrated in Figures 1 and 2. The effect of adding 0.1 and 0.2 dwb% DAC to 57 wt % zirconia suspension, shown in Figure 1, illustrates how the surfactant increases the maximum yield stress by a factor of 1.67 and 2.21, respectively. The pH of the maximum yield stress is also slightly shifted from 7.5 for pure zirconia to 8.0 and 8.5 for 0.1 and 0.2 dwb%, respectively. The shift in pH is in the direction expected for an adsorbed cationic surfactant. (Note that the pH effect shown in Figure 1 is consistent with the acid-base properties of DAC. Dodecylamine has a  $pK_a$  of 10.63 and consequently shows reduced solubility above that pH, where it exists predominantly as a neutral molecule.<sup>28</sup>) The  $\tau_y$  behavior of DTAC can be contrasted with that due to DAC. In Figure 2, the maximum yield stress is only slightly affected by the addition of 0.1 and 0.2 dwb% DTAC;  $\tau_y$  increases by a factor of 1.11 and 1.14 for this concentration range, with no significant shift in the pH of the maximum yield stress.

To probe the effect of chain length on the yielding of  $\text{ZrO}_2$  suspensions containing amine surfactants, the  $\tau_y$



**Figure 2.** Effect of the cationic surfactant DTAC on the yield stress of 57 wt % zirconia suspensions with 0.1 M KCl.



**Figure 3.** Effect of the cationic surfactant CTAC on the yield stress of 57 wt % zirconia suspensions with 0.1 M KCl.

behavior in the presence of CTAC was measured. Figure 3 indicates no significant difference between CTAC and DTAC rheology. Addition of 0.1 and 0.2 dwb% CTAC to 57 wt % zirconia suspensions increases the maximum yield stress only by a factor of 1.12 and 1.19, respectively, with no shift in the pH of the maximum yield stress. The modest effect of surfactant chain length agrees well with previous reports for long chain carboxylic acids.<sup>12</sup>

The relative effect of SDS and SDBS on the 57 wt % zirconia  $\tau_y$  is very similar to that for the pair of cationic surfactants. The effect of SDS has been reported previously: adding 0.1 and 0.2 dwb% SDS increased the yield stress by a factor of 1.69 and 3.0 and shifted the pH of the maximum yield stress to pH 4.5 and 3.8, respectively.<sup>4</sup> On the basis of charge neutralization arguments, a shift is expected for an anionic species adsorbed on zirconia. Figure 4 shows that SDBS affects the pH of the maximum yield stress in a manner similar to that for SDS. For 0.2 dwb% the pH is shifted to 5.5 while for 0.5 dwb% it moves to 5.0. However, adding SDBS does not increase the yield stress in the way found for SDS. In Figure 4, the maximum yield stress for 0.2 dwb% added SDBS is seen to increase by a factor of 1.06; the increase for 0.5 dwb% is 1.19.

The increase in yield stress relative to that of pure zirconia upon surfactant addition for the five species of interest is summarized in Table 1. Note that regardless of the species present the measured yield stress always increases upon surfactant addition, although sometimes

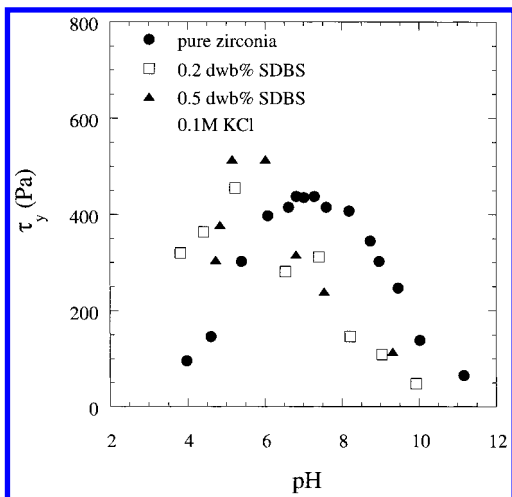
(25) O'Brien, R. W. *J. Fluid Mech.* **1990**, *190*, 81.

(26) O'Brien, R. W.; Cannon, D. W.; Rowlands, W. N. *J. Colloid Interface Sci.* **1995**, *173*, 406.

(27) Iwasaki, I.; de Bruyn, P. L. *Surf. Sci.* **1965**, *3*, 299.

(28) Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*, 72nd ed.; CRC Press: Boca Raton, FL, 1991.

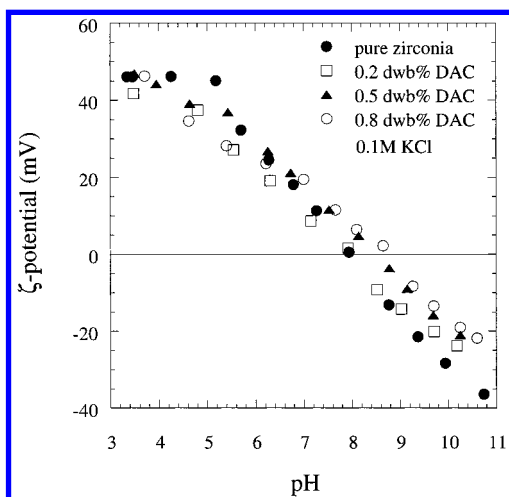




**Figure 4.** Effect of the anionic surfactant SDBS on the yield stress of 57 wt % zirconia suspensions with 0.1 M KCl.

**Table 1. Effect of Surfactant Additives on  $\tau_y$  for 57 wt % Zirconia Suspensions**

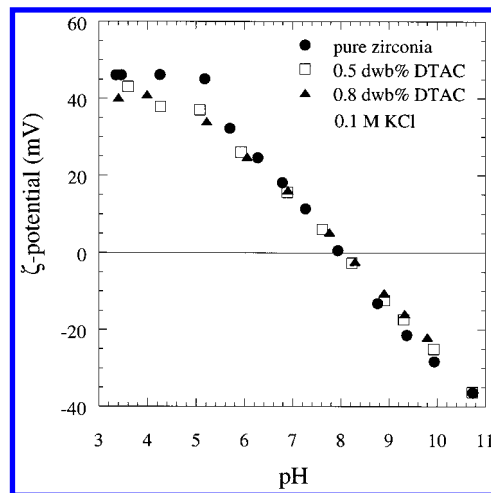
surfactant	DAC	DTAC	CTAC	SDS <sup>4</sup>	SDBS
$(\tau_y, 0.1 \text{ dwb\%})/(\tau_y, 0)$	1.67	1.11	1.19	1.69	
$(\tau_y, 0.2 \text{ dwb\%})/(\tau_y, 0)$	2.21	1.14	1.12	3.0	1.06
$(\tau_y, 0.5 \text{ dwb\%})/(\tau_y, 0)$					1.19



**Figure 5.** pH dependence of the  $\zeta$ -potential for dwb% amounts of DAC added to 2 vol % aqueous zirconia solutions.

the magnitude of the increase is comparable to experimental error.

**Electrokinetic Studies.** The effect of added DAC on the pH dependence of the  $\zeta$ -potential for zirconia suspensions is shown in Figure 5. The results for pure zirconia show a monotonic decrease in  $\zeta$ -potential as pH increases, with an IEP of approximately 7.8, in close agreement with the yield stress measurements. For the highest dwb% of DAC studied, the IEP of the surfactant zirconia mixtures is shifted to pH = 8.8. The direction of the shift is expected for a specifically adsorbed cationic species. Furthermore, the  $\text{ZrO}_2$   $\zeta$ -potential curves with added DAC in the pH range 7.8–11 are as anticipated, since both electrostatic and hydrophobic driving forces for adsorption exist in this region; the  $\zeta$ -potential changes in response to that adsorption. Additionally, hydrophobic interactions promoting adsorption must be significant given that shifts in the  $\zeta$ -potential curve in the region  $5.5 < \text{pH} < 7.8$  are observed even though in this region electrostatic interactions do not drive adsorption. The existence of a hydrophobic component of the energetics of surfactant adsorp-



**Figure 6.** pH dependence of the  $\zeta$ -potential for dwb% amounts of DTAC added to 2 vol % aqueous zirconia solutions.

tion on mineral surfaces is well established.<sup>29,30</sup> Finally, for  $\text{pH} < 5.5$  a slight decrease in the measured  $\zeta$ -potential is observed upon addition of surfactant. This decrease is most likely an artifact of the measurement, since bubbles (stabilized by cationic species in solution) were observed in the suspensions under these conditions. Experiments of this type involving the addition of surfactants are nearly always compromised by bubble formation at high surfactant addition rates.

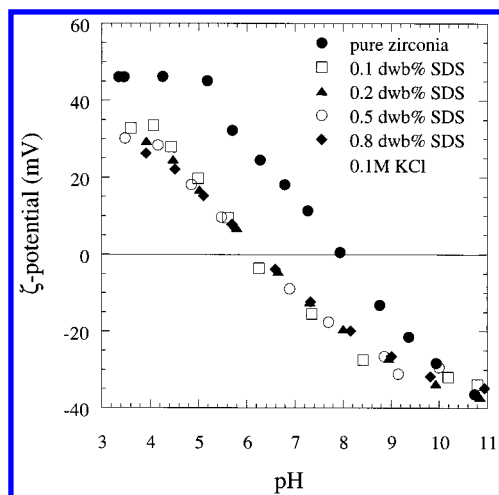
The effect of DTAC on the  $\zeta$ -potential of zirconia is qualitatively similar to that observed with DAC; however, the changes are smaller. While at 0.8 dwb% DAC the zirconia IEP is shifted by more than one pH unit, the shift is at most 0.3 pH units for DTAC. Similarly, while, at the highest pH studied, 0.8 dwb% DAC changes the  $\zeta$ -potential by approximately 15 mV, a change of only 7 mV is measured for DTAC. From Figures 5 and 6 it can be concluded that changes to the zirconia  $\zeta$ -potential due to added DAC and DTAC are modest. Additionally, in marked contrast to the yield stress measurements, only a slight difference between the effect of DAC and DTAC is observed.

The effect of SDS and SDBS on the zirconia  $\zeta$ -potential is plotted in Figures 7 and 8. Behavior analogous to that shown in Figures 5 and 6 is observed. Upon increasing surfactant concentration, the  $\zeta$ -potential is decreased over the whole pH range studied. Interestingly, the degree to which the  $\zeta$ -potential decreases is relatively insensitive to the dwb% of added anionic surfactant. At the highest concentration of SDS (0.8 dwb%) the IEP is shifted to 6.2 (from 7.8 for pure zirconia). Note that the observed  $\zeta$ -potential shifts in Figure 7 are less than the shifts to the pH of maximum  $\tau_y$  for SDS in ref 4. It is also of interest to note the specific adsorption of the SDS molecule to the zirconia surface. This may be a reflection of the surface properties of the zirconia or may be due to low level contaminants in the SDS promoting adsorption. This behavior was not observed in some of the original work of SDS adsorption to oxide surfaces.

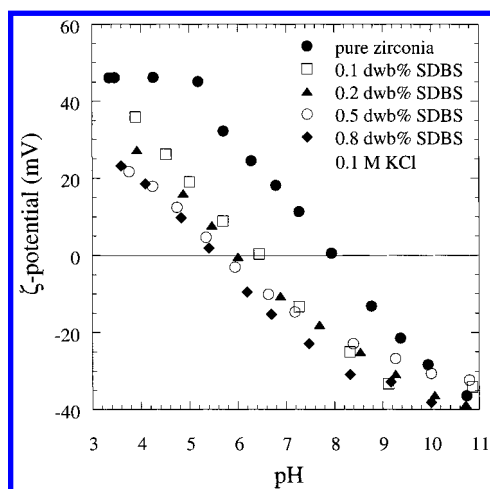
Adding 0.8 dwb% SDBS shifts the IEP by a greater amount (to 5.4 from 7.8) than SDS. The  $\text{ZrO}_2$   $\zeta$ -potential curves for added SDS and SDBS are as expected for adsorption induced by electrostatic and hydrophobic interactions. Furthermore, the slightly greater IEP shift

(29) Healy, T. W. In *Electrochemistry: the Past Thirty and the Next Thirty Years*; Bloom, H., Gutmann, F., Eds.; Plenum: New York, 1977.

(30) Hunter, R. J. *Foundations of Colloid Science*; Clarendon: Oxford, 1989; Vol II.



**Figure 7.** pH dependence of the  $\zeta$ -potential for dwb% amounts of SDS added to 2 vol % aqueous zirconia solutions.

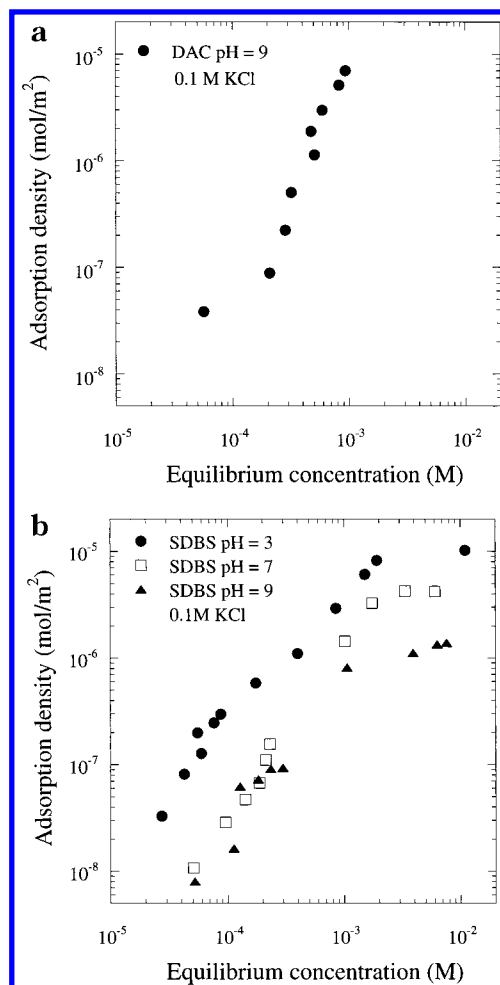


**Figure 8.** pH dependence of the  $\zeta$ -potential for dwb% amounts of SDBS added to 2 vol % aqueous zirconia solutions.

induced by SDBS than by SDS is consistent with the greater hydrophobicity of SDBS relative to SDS (as quantified, for example, by the difference in the cmc of each). Finally, Figures 7 and 8 indicate that differences in the electrokinetics of zirconia with SDS and SDBS are also not nearly as significant as those observed in the rheology.

Thus, Figures 5–8 are consistent with surfactant adsorption on the zirconia particles; however, changes to the  $\zeta$ -potential induced by this adsorption do not vary greatly within either of the cationic or anionic surfactant pairs.

**SDBS and DAC Adsorption.** The adsorption behavior of DAC at pH = 9 as well as of SDBS at pH = 3, 7, and 9 is shown in Figure 9. Results are plotted in the conventional manner; a manipulation is required to convert these figures to the dwb% of the rheological and electrokinetic measurements. For example, by means of Figure 9a it can be computed that, for DAC at pH = 9 and for the particle loadings of the rheological experiments, 0.1 dwb% DAC equilibrates to a solution concentration of  $2.3 \times 10^{-4}$  M. Similarly, 0.2 dwb% DAC equilibrates to  $3.3 \times 10^{-4}$  M. The magnitude of the adsorption observed in Figure 9a is qualitatively similar to literature reports for DAC on a different surface of approximately the same  $\zeta$ -potential.<sup>31</sup>



**Figure 9.** Adsorption density of DAC (a) and SDBS (b) on zirconia surfaces at various values of pH.

**Table 2. Adsorption Area Per Molecule of Surfactant,  $\text{\AA}^2/\text{molecule}$ , for 57 wt % Zirconia Suspensions**

surfactant	0.1 dwb%	0.2 dwb%	0.5 dwb%
DAC pH = 9	2080	830	278
SDBS pH = 3	2080	830	333
SDBS pH = 7	6180	2280	556
SDBS pH = 9	9800	2450	1190

For the case of SDBS, maximum adsorption is expected at low pH, where the zirconia and surfactant are of opposite charge. From Figure 9b it is clear that increasing pH tends to decrease the measured adsorption density. However, SDBS still adsorbs on zirconia to a significant degree at pH = 9. There is no electrostatic driving force for adsorption at this pH. This is consistent with the electrokinetic results (Figure 8) and again indicates that nonelectrostatic mechanisms play a role in surfactant adsorption on zirconia.

Of further interest in Figure 9 is the fact that the adsorptions of DAC at pH = 9 and SDBS at pH = 3 are comparable. Yet, their rheology is more dramatically different; 2.0 dwb% DAC added to zirconia increases the observed yield stress by more than a factor of 2 while SDBS at the same concentration has a much smaller effect. Figure 9 indicates that the qualitative differences in  $\tau_y$  enhancement cannot be explained by discrepancies in the degree of surfactant adsorption.

The results of adsorption measurements are summarized in Tables 2 and 3. The average area of adsorption per molecule is significantly larger than that expected for full coverage (i.e. ca.  $30 \text{ \AA}^2/\text{molecule}$ ). For a given dwb%

(31) Nishimura, S.; Tateyama, H.; Tsunematsu, K. *J. Colloid Interface Sci.* **1993**, *159*, 198.

**Table 3. Percent Degree of Full Coverage for Surfactant Adsorption for 57 wt % Zirconia Suspensions**

surfactant	0.1 dwb%	0.2 dwb%	0.5 dwb%
DAC pH = 9	0.4	1.0	3.0
SDBS pH = 3	0.8	2.0	5.0
SDBS pH = 7	0.7	1.8	7.5
SDBS pH = 9	1.3	5.0	10.8

surfactant concentration, the percent of full coverage has been computed in Table 3. The values have a large uncertainty, since the adsorption density at full coverage cannot be precisely determined from Figure 9. Additionally, an adsorption plateau was not observed for DAC at pH = 9. Consequently, the values reported for DAC at pH = 9 in Table 3 are to be taken as upper bounds to the true percent of full coverage. Nevertheless, the very low extent of surfactant coverage is apparent. Note that the low tabulated coverages are consistent with an alternate calculation assuming full coverage to be a close-packed monolayer and making a reasonable estimate of the adsorption area of a single surfactant molecule. This is the first time that the degree of surface coverage has been reported in surfactant/particulate systems exhibiting yield stress enhancement. Table 3 will be useful for relating yield stress enhancement to the underlying suspension microstructure.

### Discussion

The effect of surfactant additives on the yielding of concentrated zirconia suspensions has been found to be remarkably sensitive to the details of the surfactant headgroup chemical structure. While the measured  $\tau_y$  of pure zirconia suspensions was entirely consistent with current theories and previous experiments, the rheological, electrokinetic, and adsorption results for surfactant/particulate systems provide new insights into the mechanisms by which surfactant additives influence the rheology of concentrated mineral suspensions.

In Table 1 it can be noted that, in every instance, addition of surfactant to zirconia suspensions increased the maximum yield stress of the system relative to that of pure zirconia. van der Waals and electrostatic (DLVO) interactions alone cannot explain this observation. Specifically, the maximum yield stress of a pure zirconia suspension occurs at the material's IEP, where the system is in a state of maximum coagulation. If the adsorption of small molecules (such as surfactants) is considered only within the DLVO framework, a decrease in yield stress is expected, as the adsorbed species form a steric barrier between particles.<sup>10</sup> The resultant increase in separation between particles upon adsorption will reduce the van der Waals attraction. The system is consequently not as strongly coagulated, and a lower yield stress is observed. That surfactant additives increase the maximum yield stress instead of the expected decrease is an indication that van der Waals and electrostatic interactions cannot be the only forces determining the rheology.

Table 1 also indicates that the additional interactions or chemistry required to understand the rheology are extremely sensitive to headgroup molecular structure. That is, a primary and tertiary amine surfactant showed qualitatively different yielding behavior. Similarly, adding a phenyl ring near the sulfate headgroup of SDS significantly changed the  $\tau_y$  behavior. Interestingly, the rheology was not nearly as sensitive to the length of the surfactant chain. Our measurements with CTAC and DTAC, as well as work by Leong et al. for carboxylic acids,<sup>12</sup> demonstrate conclusively that yield stress enhancement

is not a strong function of surfactant chain length for the carbon number range 6–16.

The electrokinetic and adsorption measurements were not nearly as sensitive to headgroup chemical structure as the yield stress measurements. All the surfactants studied showed electrokinetic evidence of adsorption (although the effect of DTAC on the  $\text{ZrO}_2$   $\zeta$ -potential was modest); however, changes to the  $\text{ZrO}_2$   $\zeta$ -potential induced by the additives did not differ within the cationic and anionic pairs in the dramatic way observed in the yield stress measurements. Additionally, the two surfactants tested showed very similar adsorption densities. Unfortunately, there is little comparative data available from force studies although a number of groups have looked at interaction forces as a function of surfactant concentration.<sup>32–34</sup> The nature of the observed forces indicates that homogeneous adsorbed structures were probably not present in a number of cases although a detailed overview of the effect of headgroup is rare, as are independent electrokinetic measurements.

Although significant adsorption was observed, Table 3 demonstrates that, for additive levels in the range 0.1–0.5 dwb%, the amount of adsorption was still significantly below full coverage. It is remarkable that additives present at these modest levels of surface coverage induce profound changes to the zirconia yielding behavior. Tables 1 and 3 together demonstrate the extreme sensitivity of concentrated particulate systems to small concentrations of surfactant additives.

We now turn our attention to the origin of this sensitivity and its apparent dependence on the exact chemical structure of the surfactant headgroup. SFA and AFM results have demonstrated that under some circumstances the measured forces between surfaces with adsorbed surfactants contain an attractive component of long range ( $\sim 100$  nm).<sup>35</sup> The origin of this attraction remains unclear but has been attributed to the hydrophobicity of the surfactant chains adsorbed on the two opposing surfaces. This hydrophobicity could influence the macroscopic rheology in two ways. The free energy of a suspension in which surfactants are adsorbed on adjacent zirconia particles could be minimized by close approach of the hydrophobic surfactant constituents. Perturbations to this minimum free energy configuration induced by macroscopic deformation would result in an apparent interparticle adhesion and, consequently, a greater  $\tau_y$  than observed for pure zirconia suspensions. This mechanism was discussed earlier by Leong et al.<sup>12</sup> The results herein suggest that this mechanism cannot completely explain the observed increases in  $\tau_y$  upon surfactant addition. Specifically, since the surfactants are all similarly hydrophobic, why do DAC and SDS induce much greater yield stress enhancement than DTAC or SDBS?

Another way in which  $\tau_y$  could be influenced by surfactant hydrophobicity offers a potential explanation. Depending on the exact nature of the surface and surfactant, it has been suggested that adsorption is an aggregative phenomenon in which "hemi-micelles" are formed on the particle surface.<sup>30,36</sup> Hemi-micelles form when aggregation of adsorbed surfactants is energetically preferred to the adsorption of an isolated species. Such

(32) Yoon, R.-H.; Ravishankar, S. A. *J. Colloid Interface Sci.* **1996**, *179*, 403.

(33) Xu, Z.; Ducker, W.; Israelachvili, J. N. *Langmuir* **1996**, *12*, 2263.

(34) Parker, J. L.; Yaminsky, V. V.; Claesson, P. M. *J. Phys. Chem.* **1993**, *97*, 7706.

(35) Israelachvili, J. *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: London, 1992.

(36) Gaudin, A. M.; Fuerstenau, D. W. *Min. Eng.* **1955**, Oct, 1.

a situation occurs if surfactant hydrophobicity drives aggregation even given the unfavorable Coulombic repulsions of proximate headgroups. Interestingly, a recent AFM study of amine surfactant adsorption on mica seemingly indicates that hemi-micellar size is correlated to the degree of amine substitution.<sup>37</sup> In that study, the average size of primary and tertiary amine surfactant aggregates was found to differ by as much as a factor of 4. Thus the chemical structure of the surfactant headgroup could play a role in surfactant aggregation on surfaces. A number of additional atomic force microscopy studies have shown a key link between surfactant structure and the nature of surface adsorbed structures<sup>38,39,40</sup> although many of the surfaces where themselves hydrophobic and resolving the exact driving force for the formation of aggregates was not always clear.

A link between surfactant aggregate structure and the degree of yield stress enhancement can now be hypothesized: Since both aggregate formation and  $\tau_y$  enhancement are apparently linked to surfactant headgroup chemical structure, these two phenomena might themselves be related. AFM imaging of the aggregate structure of these surfactants on zirconia surfaces could provide

evidence in this regard. However, given the substantial roughness and heterogeneity of the zirconia surfaces, imaging the aggregate structures in question would challenge the current capabilities of AFM instruments. Furthermore, even if a connection between aggregate structure and  $\tau_y$  enhancement were established, the exact mechanism relating the two would still remain to be identified. Finally, other possibilities to be considered include the effects of heterogeneous charged surfaces,<sup>41</sup> perturbations to near-surface water structure induced by adsorbed species,<sup>4</sup> and bridging bubbles.<sup>42</sup>

Notwithstanding these tentative links to AFM measurements of surfactant aggregates, identifying surfactant headgroup chemical structure as a determinant of yielding behavior is a step toward understanding the origin of yield stress enhancement observed in certain surfactant/particulate systems. That is, current explanations of this phenomenon in terms of the effect of surfactant hydrophobicity on interparticle forces should be modified to incorporate the remarkable sensitivity of the yield stress to the chemistry of the surfactant headgroup.

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(37) Nishimura, S.; Scales, P. J.; Biggs, S. R.; Healy, T. W. *Colloids Surf., A* **1995**, *103*, 289.

(38) Manne, S.; Cleveland, J. P.; Gaub, H. E.; Stucky, G. D.; Hansma, P. K. *Langmuir* **1994**, *10*, 4409.

(39) Manne, S.; Gaub, H. E. *Science* **1995**, *270*, 1480.

(40) Wanless, E. J.; Davey, T. W.; Ducker, W. A. *Langmuir* **1997**, *13*, 4223.

(41) Miklavic, S. J.; Chan, D. Y. C.; White, L. R.; Healy, T. W. *J. Phys. Chem.* **1994**, *98*, 9022.

(42) Attard, P. *Langmuir* **1996**, *12*, 1693.