Development of Short-Range Repulsive Potentials with Short-Chain Surfactants in Aqueous Si_3N_4 Slurries

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Abstract

The effect of both cationic (n-trimethylammonium bromide, C_nTAB) and zwitterionic (phosphocholine, C_nC_nPC) surfactants on the properties of aqueous slurries of silicon nitride was studied. These surfactants were expected to adsorb to the surface of silicon nitride particles to produce short-range repulsive interparticle potentials that might be useful for the colloidal processing of advanced ceramic powders. Electrophoretic, adsorption, and viscosity measurements showed that longer chain length surfactants (C_nTAB, $n \geq 12$ and C_nC_nPC, $n \geq 9$) strongly adsorb. Surfactants with shorter chain lengths were highly soluble and did not adsorb. Although the C_nTAB, $n \geq 12$ surfactants produced very weak particle networks with a low viscosity, the packing density during consolidation was very low, and the bodies were brittle (cracked before plastic deformation). The less soluble, longer chained C_nC_nPC, $n \geq 9$ surfactants did produce high particle packing densities, but also produced brittle bodies. In all cases, it appeared that the surfactants could be pushed away from the surface during particle packing.

1 Introduction

It has been shown that colloidal processing can improve the strength of structural ceramics by reducing the size of strength degrading heterogeneities (strong agglomerates and inclusions) in the starting powder.[0,1] As best demonstrated by Pujari et al.,[2] this approach can lead to not only a significant increase in average strength, but also to a threshold strength, or, a strength below which no specimen will fail. The creation of a threshold strength demonstrates that removing heterogeneities greater than a given size is equivalent to truncating the flaw size distribution.

Heterogeneities can be removed by filtering a slurry in which the particles are highly repulsive; i.e., a repulsive interparticle pair potential is the first requirement of colloidal processing. To avoid re-introducing similar heterogeneities, the slurry can not be dried, but must be formed into an engineering shape by methods used for traditional, clay based ceramics. Clay based slurries are shaped either during consolidation by slip casting and pressure filtration or after consolidation by extrusion and forging. Consolidated clay bodies are plastic, a property generally not associated with consolidated bodies formed from advanced ceramic powders. Recent research has shown that clay-like bodies can be produced provided that a weakly attractive particle network can be developed.[3,4] The weakly attractive network achieved for some ceramic powders is produced by developing a short-range repulsive interparticle potential that partially 'shields' the pervasive, attractive van der Waals potential.

Short-range repulsive potentials can be produced in two general ways. In the first method, a surface charge is developed on each particle when neutral -M-OH surface sites are titrated with either acid or base followed by an increase in the salt concentration to produce a highly compressed cloud of counterions. The particles are attractive due to van der Waals forces until their counterion clouds begin to interact.[5] The increase in counterion concentration between the particles increases the free energy causing a repulsion at short separation distances. This approach is effective for colloidal processing because at low salt concentrations the particles can be highly repulsive, which is needed to first filter the heterogeneities from the slurry. After filtration, salt can be added to compress the counterion clouds and produce the desired short-range repulsive potential.

In the second method, molecules are either phys- or chem-adsorbed on the surface of the particles. The 'brush' of molecules that protrudes from the surface

must be short so that the van der Waals attractive potential is not fully screened. Decreasing the separation distances necessitates a compression of the 'brushes' which increases the free energy of the system and thus produces a repulsive potential. The equilibrium separation distance can be approximated by twice the 'brush' thickness (twice the molecular length).[6]

Silicon nitride is a leading candidate for high temperature structural applications due to its low thermal expansion coefficient and modest elastic modulus, which minimize thermal stresses that might develop during thermal transients.[6] In addition, it develops a fibrous microstructure during processing that imparts high fracture toughness, and thus, a potential for high strength.[7] As detailed elsewhere,[8] the approach of using a compressed counterion cloud to produce a short-range repulsive potential is effective in the slurry state, but the potential is insufficient to keep the particles from being pushed together during particle packing and thus a brittle, consolidated body is formed. Kramer and Lange [4] showed that different alcohols could be reacted with the -Si-OH surface sites to chemically bond hydrocarbon chains to the surface of silicon nitride particles. The strength of saturated, consolidated particle networks was shown to be inversely proportional to the length of the hydrocarbon chain. Longer hydrocarbon chains kept particles farther apart by truncating the van der Waals attraction at a greater separation distance. Kramer and Lange showed that consolidated bodies with a high particle packing density could be plastic after consolidation with a yield stress that could be altered by changing the length of the bonded hydrocarbon chain.

Although the method of Kramer and Lange [4] was shown to produce the desired viscosity and consolidated body behavior, there are several reservations associated with this method. First, this method yields hydrophobic particles, and thus, a non-aqueous liquid must be used to formulate a slurry. A second, more serious concern, is that the alcohol has to be reacted with the particles before they can be dispersed and filtered to remove heterogeneities. That is, the method of reacting the powder with alcohol is not compatible with the need to first produce a long-range, repulsive potential required for filtration.

It is well known that surfactant molecules can adsorb on the surface of particles to control the interparticle pair potential.[9,10] Above the critical micelle concentration (cmc), surfactant molecules aggregate to form structures such as micelles, vesicles and bilayers. Below the cmc, the surfactant is in solution as a monomer. The cmc and the type of structure formed are specific to a surfactant and are governed by both the solubility and the geometry (size and charge of the head-

group and length of the hydrocarbon tail).[6] These structures form to maximize the contact of the hydrophilic head-group with water. When hydrophilic ceramic powders are present, the surfactant is expected to adsorb to the particle surface. Recent AFM studies show that above the cmc, adsorbed surfactant adopts a morphology which is surface dependent.[11] For the limited surfactant/surface interactions studied to date, surfactants that form micelles in solution, appear to adsorb to particle surfaces as micelles; i.e., a micelle former will not adsorb to a surface as a bilayer. At concentrations far below the cmc, studies indicate[12] that hydrophilic surfaces can become hydrophobic in the presence of the surfactant, suggesting that a surfactant has adsobed as a monolayer. Further, for other surfacants, it has been[13] shown that bilayers can form on surfaces at concentrations below the cmc. At higher concentrations, the particle surface can be covered by one bilayer or more bilayers.

Two different surfactants were investigated in the current study: cationic surfactants (C_8TAB, octyltrimethylammonium bromide and its homologues) and zwitterionic surfactants (C_6C_6PC, 1,2-dihexanoic-sn-glycero-3-phosphocholine and its homologues). Rheological measurements were used to determine the presence of a short-range repulsive potential in slurries with added surfactants. Complimentary experiments, published elsewhere, were carried out to confirm the existence of a short-range repulsion between silicon nitride surfaces in the presence of phosphocholine with the atomic force microscope.[13,14] Adsorption isotherms determined the amount of surfactant required for surface coverage. Consolidation experiments were conducted to determine if the packing density was affected by the adsorbed surfactants. The mechanical behavior of the consolidated body was examined. As detailed below, high packing densities were achieved with slurries formulated with zwitterionic surfactants.

2 Experimental Procedure

2.1 Surfactants

Octyltrimethylammonium bromide (C_8TAB)[a] and three homologues ($C_{10}TAB$, $C_{12}TAB$ and $C_{16}TAB$)[a] were used as-received and added to silicon nitride slurries. CnTAB surfactants form micelles in solution at moderate concentrations above the cmc and are known to form cylinders on mica surfaces.[12] The head-group of all of these surfactants is identical, whereas the subscript refers to the number of

carbon units in the surfactant tail (e.g., C_8TAB has 8 carbon units). In water, the bromine ion on the head-group dissociates at all values of pH to produce a positively charged head-group. The zwitterionic surfactants, C_6C_6PC (1,2-dihexanoic-sn-glycero-3-phosphocholine)[b] and its homologues[b] (also used as-received) possess two tails and two oppositely charged head-groups. These lipids form vesicles, i.e., spherical configurations with bilayer walls, in solution and are expected to form bilayers on surfaces because of the two hydrocarbon tails. At concentrations greater than the cmc, phosphocholine surfactants with 8 or less carbon units in each tail form vesicles in solution whereas phosphocholines with chains longer than 8 carbon units only form bilayers in water.[15]

2.2 Adsorption Determinations

Surfactant adsorption was characterized by either zeta potential measurements or measurements of the adsorption isotherms. Adsorbed cationic surfactants were expected to shift the iso-electric point (iep) of Si_3N_4.[16] That is, the cationic surfactant molecules have a positively charged head-group which could be attracted to the dominant negative surface sites of Si_3N_4 particles at pH values > 5 (the iep of Si_3N_4). Thus, zeta potential measurements were used to determine the adsorption behavior of the cationic surfactants. Although the zeta potential of the zwitterionic surfactants was measured, their adsorption behavior was also determined by a colorimetric [17] method described below.

For zeta potentials measurements, dilute suspensions of silicon nitride [c] (mean particle diameter of 0.8 μm by Sedigraph [d] and surface area of 3.2 m^2/g by BET [e]) were prepared in deionized water (14 MΩ) by ultrasonication. [f] These specimens were allowed to equilibrate for ~24 hours on a shaker. Specimens prepared for zwitterionic surfactant addition were adjusted to pH 10 prior to the addition of 1 mM of the various lipids which were allowed to adsorb for a period of ~24 hours. The zeta potential of the dilute slurries formulated with the zwitterionic surfactants was determined as a function of pH with a ZetaPlus instrument. [g] Since the pH of slurries formulated with the cationic surfactants changed with surfactant addition, they were equilibrated for ~1 hour before the zeta potential was determined as a function of pH using a Zetameter. [h] pH adjustments were made with either HNO_3 or KOH.

Adsorption isotherms were only determined for the zwitterionic surfactants. Slurries containing 4.5 g of silicon nitride and 45 mL of deionized water were

dispersed by ultrasound. The pH was adjusted to 10 and the specimens allowed to equilibrate for ~24 hours on a shaker. Zwitterionic surfactant additions were made and the samples were allowed to equilibrate for another ~24 hours on a shaker. The pH of the specimens was adjusted, if necessary. If the pH was significantly adjusted; e.g., from pH 10 to 6, the specimen was left to equilibrate for at least one hour. To separate the liquid from the particles, the specimens were centrifuged [i] at 1,600 RPM for 10-20 minutes. To remove residual particles that would scatter light, the supernatant was centrifuged [j] at 18,000 RPM for 30 minutes.

After centrifugation, the supernatant (0.2, 0.5 or 1 mL) was used to determine the quantity of unabsorbed surfactant molecules with the following procedure.[18] Deionized water was added to produce a total water volume of 1 mL. 2 mL of 1 N ammonium ferrothiocyanate (a dye) and 4 mL of chloroform were added and vigorously shaken for 1.5 minutes. The surfactant, now complexed with the dye, was solubilized in chloroform; the excess, unreacted dye which is not soluble in chloroform, remained in the water. The chloroform solution was separated to determine its adsorption using a colorimeter [k] set to a wavelength of 466 nm. The adsorption of each specimen was compared with a calibration curve to determine the quantity of surfactant remaining in the supernatant. The difference between the amount added to the specimen and the amount remaining in the supernatant was taken to be the amount adsorbed to the powder.

Calibration solutions were produced by dissolving a known quantity (~20 mg) of phosphocholine in 100 mL of chloroform (the standard). In a test tube, 1 mL of deionized water, 2 mL of 1 N ammonium ferrothiocyanate, a known amount of the standard and enough pure chloroform to total 4 mL were combined and shaken for 1 minute. The chloroform was then removed and its adsorption of light with a wavelength of 466 nm was measured.

2.3 Slurry Preparation

Slurries containing a known volume fraction of powder were prepared by dispersing silicon nitride powder in deionized water by ultrasound. The pH of these suspensions was adjusted with either HNO_3 or KOH. All specimens were equilibrated for ~24 hours on a shaker followed by pH adjustment, if necessary, prior to surfactant addition. Surfactant was added to the slurry and allowed to dissolve for ~30 minutes at which time the pH was again adjusted and left for ~30 minutes prior to characterization.

2.4 Rheological Measurements

Viscosity measurements were made with an RMS-800 [1] rheometer using a coni-cylinder tool. The coni-cylinder geometry consisted of concentric cylinders with a 1 mm gap, 25 mm radius and a length of 77 mm. Slurries were first characterized at a high shear rate (1000 s^{-1}) to break up any initial network structure and then at decreasing shear rate until the torque was below the sensitivity of the instrument (1 g-cm). Changes in equilibration time (from 60 s to 180 s) between measurements did not affect the viscosity.

2.5 Consolidation

Pressure filtration was used to consolidate the slurries (2, 4 or 15 MPa) with a pressure filter device described elsewhere.[18] Slurries were also consolidated by centrifugation [i] (either 0.01 MPa or 0.035 MPa) and sedimentation (180 Pa). The forming pressure for centrifugation and sedimentation was calculated for the bottom of the vessel. The relative density of the consolidated bodies was determined by weighing the specimen when saturated with water and after drying. The difference in weights was attributed solely to water. The relative density is calculated by dividing the dry volume, i.e., dry weight divided by 3.18 g/cc (the theoretical density of silicon nitride), by the volume of water plus the dry volume. In some cases, the samples were heated to 400 °C for 1 h to determine the contribution of the surfactant to the density of the specimen.

3 Results

3.1 Cationic Surfactants

Figure 1 shows the shifts in iso-electric point (iep) and zeta potential of the silicon nitride suspensions formulated with the C_nTAB homologues. Since the head-groups of all of the surfactants are identical, the different behavior was initially unexpected, but it is apparently indicative of the competition between surfactant adsorption and its solubility in water, which is a function of hydrocarbon chain length as discussed below.[17] The shortest surfactant, C_8TAB, has little influence on the zeta potential of silicon nitride (pH 5). The intermediate length

surfactants, $C_{10}TAB$ and $C_{12}TAB$, affect the magnitude of the zeta potential and increase the iep to pH 8. Because of its strong adsorption, the longest surfactant, $C_{16}TAB$, produced a positive zeta potential over the entire range of pH explored.

The rheology of slurries formulated with the various C_nTAB homologues is shown in Fig. 2. All of the slurries exhibit shear thinning except for $C_{16}TAB$. The Newtonian behavior of the slurry formulated with the longest surfactant, $C_{16}TAB$, indicates that it produces a long-range repulsive, interparticle potential. The viscosity at any strain rate decreased as the chain length of the added surfactant increased. Table 1 shows that the packing density is low for all of the slurries formulated with the C_nTAB surfactants at pH 10, but the packing density increases with increasing chain length. All consolidated bodies were brittle, (cracked before plastic deformation), suggesting that the repulsive, short-range interparticle potential developed by surfactant adsorption was removed during consolidation.

3.2 Zwitterionic Surfactants

The adsorption isotherms of the phosphocholine surfactants with different hydrocarbon chain lengths are shown in Figs 3 and 4. In all cases, the solid data points refer to adsorption isotherms for 3 vol% silicon nitride suspensions at pH 6 whereas the open circles refer to isotherms determined with a solids loading of 20 vol%; the latter data is directly compared with the rheology measurements. It should be noted that the shorter surfactants, C_6C_6PC (not shown), C_7C_7PC and C_8C_8PC, have isotherms with finite slopes as seen in Fig. 3. The finite slope indicates that only some of the surfactant adsorbs to the surface and some remains in solution. Table 2 lists the cmc of these lipids.[19] In the case of C_6C_6PC, the cmc is so high (cmc = 15 mM) that it was never attained in our experiments. At their cmc's, the surfactants C_7C_7PC (cmc = 1.4 mM) and C_8C_8PC (cmc = 0.27 mM) appeared to reach an adsorption plateau indicating that full surface coverage was attained.[20,21] Whereas the slopes of the C_6C_6PC and C_7C_7PC isotherms were nearly identical, the slope for the C_8C_8PC isotherm was steeper. In contrast, C_9C_9PC and $C_{12}C_{12}PC$ adsorb very strongly to the silicon nitride surface as shown in Fig. 4. For C_9C_9PC, adsorption was complete at the cmc (2.9×10^{-5} M). The cmc of $C_{12}C_{12}PC$ is not reported in the literature, but is estimated to be 1×10^{-7} M,[20] a concentration that is below the limit of our technique. For all surfactants, complete surface coverage appears to be reached at the cmc. For the shorter, more soluble surfactants, excess surfactant exists in solution. For the less soluble surfactants, C_9C_9PC and $C_{12}C_{12}PC$,

more surfactant appears to adsorb to the surface above their cmc. Adsorption isotherms at pH 10 were performed for C_6C_6PC, C_7C_7PC and C_9C_9PC. In all cases the difference in adsorption at pH 6 (shown) and pH 10 (not shown) was minimal.

Figure 5 shows the zeta potential as a function of pH for silicon nitride formulated with the phosphocholines. Significant differences are evident as the chain length increases from 6 to 12 carbon units. The shortest surfactant (C_6C_6PC) does not appear to have any effect on the zeta potential despite the fact that its concentration should be sufficient to cover the particle surface. Since these surfactants are zwitterionic, no observed change in the iep was expected. However, the addition of C_7C_7PC increases the iep of the powder from 5 to 7.5. C_9C_9PC slightly increases the iep (pH 5 to 6); it also significantly decreases the magnitude of the zeta potential, particularly at pH values above the iep. $C_{12}C_{12}PC$ lowers the magnitude of the zeta potential at pH values > iep.

The addition of C_6C_6PC to Si3N4 slurries has a minor effect on the viscosity (not shown), sequentially decreasing the viscosity over most of the shear rate regime by only an order of magnitude with increasing concentration (10 mM to 90 mM). Figure 6 shows the effect of the C_7C_7PC surfactant on the viscosity (pH 6, 20 vol%) as a function of the surfactant concentration; the effect of C_9C_9PC and $C_{12}C_{12}PC$ surfactants was nearly identical to C_7C_7PC. For the C_7C_7PC and C_9C_9PC surfactants, the viscosity significantly decreases for surfactant additions between 10 and 15 mM and does not change for concentrations > 15 mM; this transition occurred at a lower concentration (5 mM to 10 mM) for the longer $C_{12}C_{12}PC$ surfactant. These transition concentrations are consistent with the isothermal adsorption data (the open circles in Fig. 4) showing that, at the transition concentrations, the surfactant fully covers the surface. To obtain the same reduction in viscosity for a 40 vol% slurry (not shown), approximately twice the surfactant was needed to produce the same effect as observed for the slurry containing 20 vol% powder. These data show that a two fold increase in the surface area of the silicon nitride powder requires twice the amount of surfactant (20 mM to 40 mM) to fully cover the surface.

Figure 7 shows the effect of pH on the viscosity of slurries with adsorbed $C_{12}C_{12}PC$ at a concentration of 10 mM, the concentration just sufficient to produce a low viscosity at pH 6. At pH 2 and pH 10, the slurry is Newtonian (shear rate independent) showing that the particles are highly repulsive at pH 2 and 10, relative to the weakly attractive (shear thinning) behavior for pH values between 4 and 8. These data are consistent with the high values of zeta potential shown in Fig. 5 at

high and low pH. Despite similar adsorption characteristics at pH 6 and at pH 10, the viscosity data in Fig. 7 shows that at both pH 2 and 10, the particles are repulsive. Since the adsorbed bilayer does not produce charged sites, the electrostatic behavior of the particles must be due to charged surface sites on the Si_3N_4 surface itself.

Table 3 shows the packing density of bodies consolidated from the slurries formulated with zwitterionic surfactants of differing chain lengths at pH 10 (dispersed) and pH 6 (flocced). Slurries containing particles with the partially adsorbed C_6C_6PC surfactant had the lowest packing density, which was a few percent lower than for a slurry without any adsorbed surfactant flocculated at pH 6. The highest packing density was obtained for slurries containing the adsorbed C_9C_9PC surfactant. Although the $C_{12}C_{12}PC$ surfactant also produces a high relative density, it was lower than the shorter C_9C_9PC surfactant, and, being a surfactant with a higher molecular weight, resulted in a larger weight loss when the surfactant was removed from the powder compact by pyrolysis.

Figure 8 shows the behavior of slurries formulated with C_9C_9PC or $C_{12}C_{12}PC$, consolidated by various forming pressures. Except for slurries which were allowed to settle, the packing densities are not greatly pressure sensitive. In all cases, slurries with C_9C_9PC packed to slightly higher density relative to slurries formulated with $C_{12}C_{12}PC$. Although the pressure filtered bodies were brittle, the top portion of the centrifuged samples would flow under the force of gravity.

4 Discussion

4.1 Cationic Surfactants

Cationic surfactants were chosen for this study with the hypothesis that at a pH above the iso-electric point (iep) of Si_3N_4 (pH_{iep} = 5), the positive head-group of the cationic surfactant would strongly bind to negative surface sites to produce a strongly adsorbed layer and the short-range repulsive potential needed for a weakly attractive particle network. Zeta potential determinations (Fig. 1) show that contrary to our initial hypothesis, the solubility of the surfactant governed the adsorption behavior rather than the preference of the positive head-group for negative surface sites. C_8TAB, the surfactant with the shortest tail, did not change the iep of Si_3N_4, whereas the molecule with the longest chain length ($C_{16}TAB$) changed the iep to a pH above 11 consistent with the expectation of strong adsorption and a potential determining head-group. The connection between

adsorption and chain length can be related to the molecule's solubility in water which is highest for smaller molecules. As the solubility of the surfactant decreases, the surfactant will find it more energetically favorable to adsorb to the particle surface than remain in solution. Since the surfactant is positively charged, the head-groups facing the surface will neutralize the negative surface, whereas head-groups facing the water will produce a particle with a net positive charge.

All but $C_{16}TAB$ produced shear thinning behavior. Shear thinning behavior is generally attributed to a slurry with an attractive particle network.[22] As discussed elsewhere,[23] the greater the interparticle attraction, the greater the viscosity at any given shear rate. The viscosity of slurries with C_8TAB was very high, i.e., as high as for a slurry at its iep with no added surfactant because, due to its high solubility in water, C_8TAB does not adsorb to the surface of silicon nitride. $C_{10}TAB$ lowers the viscosity of a slurry compared with C_8TAB because it adsorbs more strongly to the surface due to its lower solubility.

In addition to the effect that relates solubility to surface coverage and viscosity, several researchers[4,24] have noted that increasing the chain length of adsorbed molecules also decreases viscosity by producing a weaker attraction between particles. In the current case, this effect would be attributed to the truncation of the van der Waals attraction at larger separation distances with longer surfactant molecules. Adding $C_{12}TAB$ lowers the viscosity much more than $C_{10}TAB$ despite the fact that the magnitude of the zeta potential is higher for $C_{10}TAB$. This observation suggests that, although the adsorbed $C_{10}TAB$ layer apparently produces a greater surface charge density, the thicker $C_{12}TAB$ layer truncates more of the van der Waals potential and thus produces a weaker particle network. The viscosity data shows that the addition of $C_{16}TAB$ produces Newtonian behavior which is evidence that the interparticle separation distance produced by two adsorbed layers of $C_{16}TAB$ was sufficient to completely shield the attractive van der Waals potential.

Silicon nitride slurries containing C_nTAB homologues packed to low relative densities. The packing density was lowest for the C_8TAB which does not adsorb. As the chain length increased, the packing density increased; nevertheless, the packing density for slurries formulated with $C_{16}TAB$ was still low relative to the zwitterionic surfactants. Since the zeta potential data indicated that $C_{16}TAB$ was adsorbed, we conclude that the surfactant was only weakly adsorbed and that it was pushed away as the particles were compressed during consolidation. In order for

the packing density to be so low, the particles must become strongly attractive at an early stage of consolidation.

The removal of the surfactant during consolidation might be attributed to an insufficient electrostatic attraction of the trimethylammonium head-group for the particle surface. In addition, the configuration of the adsorbed surfactant layer may also contribute to its lack of cohesion. Because of the similar surface charge of mica and silicon nitride within the pH range studied, the adsorption of the C_nTAB surfactants on silicon nitride may be similar to the close-packed cylindrical configuration observed on mica surfaces.[12] In contrast, the zwitterionic surfactants adsorb as bilayers. It is expected that bilayers are more robust to removal during consolidation than the cylindrical configuration.

4.2 Zwitterionic Surfactants

Zwitterionic phosphocholines (C_nC_nPC) studied in this work form either micelles ($n \leq 8$) or lyotropic liquid crystals ($n \geq 9$) in solution above their cmc. Most probably the shorter chain surfactants which form micelles in solution adsorb in the form of patchwise amorphous aggregegates, first filling the monolayer and then adsorbing in the second layer. In this way, the molecular environment of the adsorbed surfactant is constantly changing with increasing surfactant concentrations. Liquid crystal forming surfactants have such a low cmc that they adsorb in the form of two dimensional bilayers at all concentrations.[16] The molecular environment of such adsorbed surfactant aggregates does not change with increasing surface coverage. Miller and coworkers[25] used attenuated total reflectance (ATR)/FTIR spectroscopy to show that in the case of classical micellar surfactants the environment of the adsorbed surfactant changes with the increase in surfactant concentration. In an upcoming paper, we use the same strategy, namely we analyze the change in the vibrational bands frequencies of CH2 groups from the surfactant chains in order to show the environment of the adsorbed phosphocholine surfactants. Indeed, we show that the increase in concentration of C_7C_7PC is followed by a change of the CH2 frequencies of the adsorbed surfactant on a silicon nitride wafer. No change in the FTIR absorption bands frequencies of the CH2 groups from the adsorbed surfactant chains is observed for C_9C_9PC or $C_{12}C_{12}PC$, indicating the same environment (liquid crystal like surface aggregates). These results will be presented elsewhere.

Harwigsson and coworkers[26] and Chorro and coworkers[27] recently studied the adsorption of zwitterionic surfactants at the silica/water interface. They used single chain surfactants which

showed very weak interactions with the surface. Significant adsorption was observed only after the surfactant cmc was reached. Surfactants adsorbed very poorly at low pH's where the zwitterionic molecules became cationic with the same sign of charge as the surface. This indicated some electrostatic interactions between surfactant ions and the surface. The affinity of the surfactant for the surface and its solubility rather than surfactant self-assembly in solution seemed to govern the adsorption process. Chavez and coworkers[28] studied the interactions between zwitterionic surfactants and zwitterionic solids. As in our work, they found very mild pH dependence of the zwitterionic surfactant adsorption. Short chain surfactants studied by Chavez and coworkers adsorbed through the mechanisms similar to that of anionic surfactant adsorption (monolayer, second layer, full bilayer).

Similar to the cationic surfactants, adsorption studies of the zwitterionic, C_nC_nPC, surfactants showed that the shorter, more soluble molecules ($n \leq 8$) required high concentrations to fully adsorb, whereas the less soluble surfactants ($n \geq 9$) were fully adsorbed at low concentrations. Our studies strongly suggest that adsorption will not be complete until the surfactant concentration exceeds the cmc, which for the shorter surfactants, is too large to be practical for colloidal processing. For $n = 12$, data shows that adsorption is complete at very low concentrations (cmc is very small) and as more surfactant is added, adsorption continues, possibly due to some rearrangement of the bilayer or the formation of a second bilayer on top of the first.

The amount of surfactant needed to cover the powder can be estimated with knowledge of the dimensions of the surfactant molecule and the surface area of the powder. The projected area of a phosphocholine head-group is approximately 0.5 nm^2.[16] Because adsorption occurs as a bilayer, complete surface coverage requires two molecules per head-group area, or for phosphocholine, 6.6×10^{-10} moles/cm^2. Based on these estimates, the amount of phosphocholine surfactant needed to cover the surface of the Si_3N_4 powder used in this study in a 20 vol% slurry would be ~ 10 mM. This estimate is consistent with the observed adsorption isotherms. However, the size of the head-group can depend on the chain length and might range between 0.5 and 0.7 nm^2,[16] so the estimates of surface coverage can differ by at least a factor of two.

Because the zwitterionic surfactant molecules have closely spaced cationic and anionic head-groups, they are expected to adsorb on closely spaced and oppositely charged surface sites. For this reason, they are not expected to change the iep. C_6C_6PC affects neither the iep nor the magnitude of the zeta potential and

therefore can only be weakly adsorbed. As expected, the strongly adsorbing $C_{12}C_{12}PC$ does not change the iep but does change the magnitude of the zeta potential and therefore must adsorb in order to neutralize charge. The rheological behavior at different values of pH for slurries formulated with $C_{12}C_{12}PC$ is consistent with the expected surface charge density of Si_3N_4. At low and high pH (pH 2 and 10) where the surface charge is positive and negative, respectively, and the as-received particles are highly repulsive, the slurries are Newtonian (shear rate independent) with a low viscosity. Newtonian behavior is only exhibited by dispersed slurries. Whereas at pH values closer to the iep for Si_3N_4, the slurry is weakly attractive, as expected. At pH 6, the adsorbed bilayer significantly reduces the strength of the particle network relative to the network formed from slurries with no surfactant. Since the adsorption isotherms were the same at pH 6 and 10, the viscosity data strongly suggest that the charge density on the Si_3N_4 particles with an adsorbed bilayer, is similar to the as-received particles. Why the C_7C_7PC and C_9C_9PC surfactants change the iep is unclear. It can only be hypothesized that either the physics of the zwitterionic surfactant is not as simple as stated above, or the surfactant solutions contain 'impurities', e.g., potential determining ions, that inadvertently altered the electrophoretic behavior of the powder.

The relationship between adsorption and viscosity for the zwitterionic surfactants is the same as discussed above for the cationic surfactants, i.e., for concentrations < cmc, the viscosity is high at all shear rates indicative of a strong, flocced network usually observed for this powder at or near the iep. The viscosity significantly decreases for surfactant concentrations $\geq$ cmc, indicating that complete surface coverage is needed to produce a weakly attractive particle network, relative to the strong network developed at concentrations < cmc. All of the fully adsorbed zwitterionic surfactants, regardless of chain length, exhibit approximately the same rheology (same viscosity over the shear rate regime investigated). This indicates that even the shortest surfactant creates a bilayer that is large enough to screen much of the attractive van der Waals potential between particles.

Packing density is related to the particle pair potential and the slope of the repulsive potential (i.e., repulsive force). Provided they survive the rigors of particle packing, short-range repulsive potentials seem to act as a 'lubricating' force allowing particles to rearrange during consolidation.[29] Strongly attractive, touching particles have a high coefficient of friction and do not pack to high density. Partial surface coverage by a surfactant results in an attraction which is too large for rearrangement due to the hydrophobic effect. The packing densities of slurries

containing zwitterionic surfactants are listed in Table 3. Slurries formulated with C_6C_6PC consolidated to a low relative packing density. This was due to either low surface coverage by the surfactant or desorption during consolidation. In contrast, the addition of C_7C_7PC resulted in an increased packing density at concentrations where a full bilayer covers the surface. The highest packing density was attained using C_9C_9PC. This is because, although an equivalent short-range repulsion appears to develop in both C_7C_7PC and C_9C_9PC based on the viscosity data, C_9C_9PC is less soluble and therefore more difficult to remove from the particle surface,[14] as discussed below.

Although slurries formulated with longer zwitterionic surfactants did produce high packing densities, the bodies were not sufficiently plastic for extensive testing. Bodies that were compressed in a mechanical testing machine fractured before plastic flow. As detailed by Franks and Lange[30], despite the presence of either long- or short-range repulsive potentials in the slurry state, particles can be pushed together during consolidation when the consolidation pressure exceeds a critical value, i.e., when the Hertzian stress at particle contacts exceeds a critical value. For the surfactant systems studied here, the ease with which the bilayer can be pushed away will depend on its binding strength to the particle surface. The binding strength of the adsorbed surfactant depends on factors that include the electrostatic attraction between particle surface and head-group, the chemical affinity of the head-group for the surface and the solubility of the surfactant in the surrounding liquid relative to its free energy of adsorption.[31] The latter factor, the surfactant's affinity for the liquid, i.e., its solubility, appears to be one of the controlling features that distinguish the more soluble cationic surfactants from the less soluble zwitterionic surfactants of equivalent tail lengths. Atomic Force Microscopy studies [14,15] have shown that the shorter, more soluble C_7C_7PC surfactant could be pushed off of opposing silicon nitride surfaces, whereas the larger, less soluble surfactant, C_9C_9PC, could not be pushed away by the highest force that could be applied by the instrument. It is thus expected that the more soluble cationic surfactants are pushed away during particle packing, resulting in higher friction, lower particle packing and brittle bodies. The less soluble, more strongly binding zwitterionic surfactants nearly provide the desired properties, that is, they lead to high particle packing density, but they can be removed from the surface and therefore do not produce plastic bodies.

5 Conclusions

The highly soluble, short-chained surfactants studied here do not adsorb strongly to the surface of Si_3N_4, and thus do not greatly contribute to the interparticle pair potential. Electrophoretic and viscosity measurements show that cationic surfactants (C_nTAB) with longer hydrocarbon chains ($n \geq 12$) produce repulsive, interparticle potentials in the slurry state, but these molecules are easily pushed away during particle packing. Less soluble, zwitterionic surfactants (C_nC_nPC) with two, long tails ($n \geq 9$) lead to high particle packing density, but do not produce plastic consolidated bodies. It is concluded that surfactants with low solubilities that bind more strongly to the Si_3N_4 surface, e.g., by chemical bonding, are needed to produce the short-range repulsive potential need for both high particle packing density and the plastic body rheology needed for shape forming of advanced ceramic powders.

Footnotes

a   Lancaster Synthesis, Inc., Windham, NH.

b   Avanti Polar Lipids, Inc., Alabaster, AL.

c   SN-E3, Ube Industries, Ltd., New York, NY.

d   Model 5000ET, Micromeritics Instrument Corp., Norcross, GA.

e   Model ASAP 2000, Micromeritics Instrument Corp., Norcross, GA.

f   Model W-380, Heat Systems Ultrasonics, Inc. Farmingdale, NY.

g   ZetaPlus, Brookhaven Instruments, MA.

h   System 3.0, Zetameter, Inc., Long Island City, NY.

i   International Equipment Co., Boston, MA.

j   Sorvall RC-5B, DuPont, Wilmington, DE.

k   Model 340 Spectrophotometer, Sequoia-Turner Corporation, Mountain View, CA.

l   Model RMS-800, Rheometrics, Inc., Piscataway, NJ.

Table 1
Relative Packing Density of Pressure Filtered Slurries
with added Trimethylammonium Bromides at pH 10
(4 MPa)

	0.1M	0.05 M
C_8TAB	45.7%	45.0%
$C_{10}TAB$	48.1%	44.9%
$C_{12}TAB$	49.3%	47.7%
$C_{16}TAB$	51.6%	50.6%

Table 2
Critical Micelle Concentration of Phosphocholines[20]

	cmc (M)
C_6C_6PC	1.5×10^{-2}
C_7C_7PC	1.4×10^{-3}
C_8C_8PC	2.7×10^{-4}
C_9C_9PC	2.9×10^{-5}
$C_{12}C_{12}PC$	$\sim 1 \times 10^{-7}$

Table 3
Relative Packing Density of Pressure Filtered Slurries
with added Phosphocholine
(4 MPa)

	Before Burnout	After Burnout
SN-E3 (pH 10, 0 M)	60%	----
SN-E3 (pH 6, 0M)	47%	----
C_6C_6PC (pH 6, 50 mM)	46.4%	----
C_7C_7PC (pH 6, 30 mM)	55.3%	54.4%
C_9C_9PC (pH 6, 30 mM)	59.7%	58.5%
$C_{12}C_{12}PC$ (pH 6, 30 mM)	57.9%	55.5%
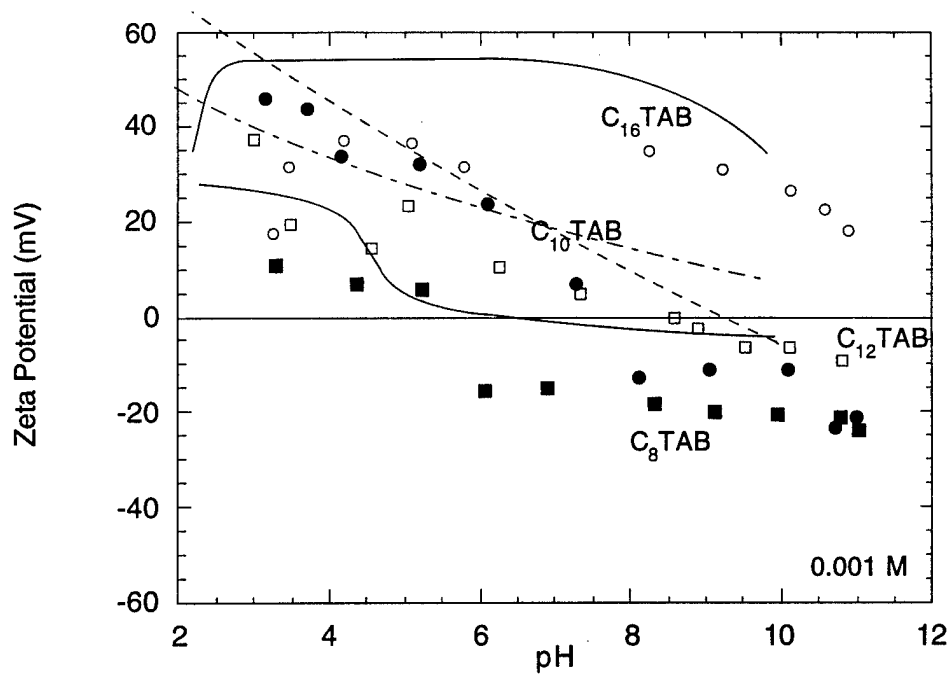
Figure 1   The effect of different chain length C_nTAB homologues on the zeta potential of silicon nitride. (Lines are added to guide the eye.)
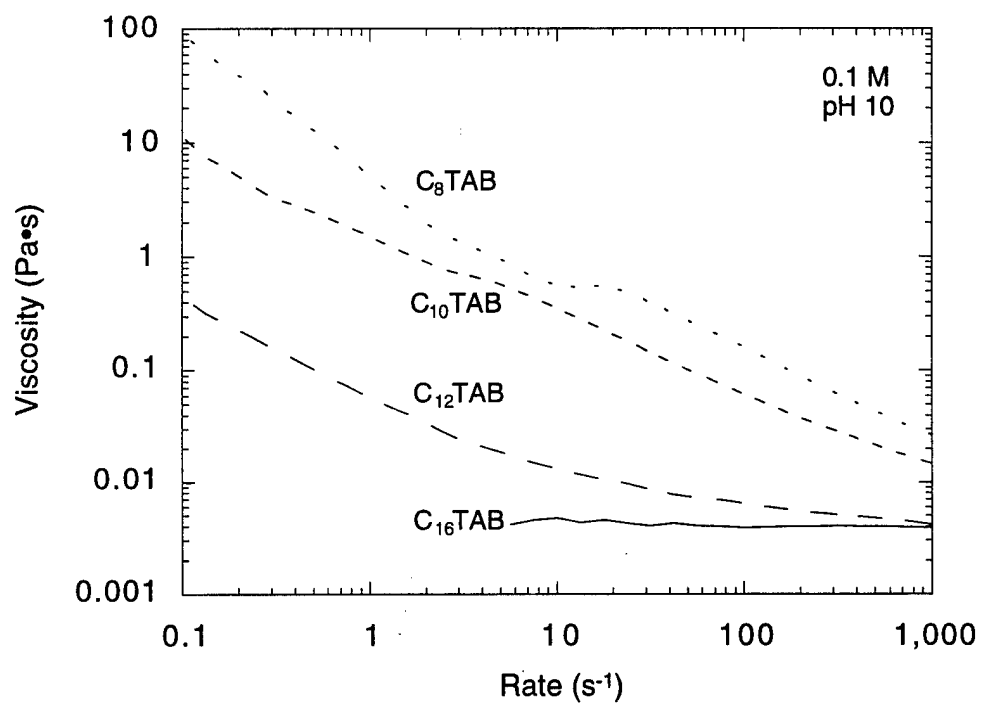
Figure 2 The rheology of silicon nitride slurries (20 vol%) to which C_nTAB homologues have been added.
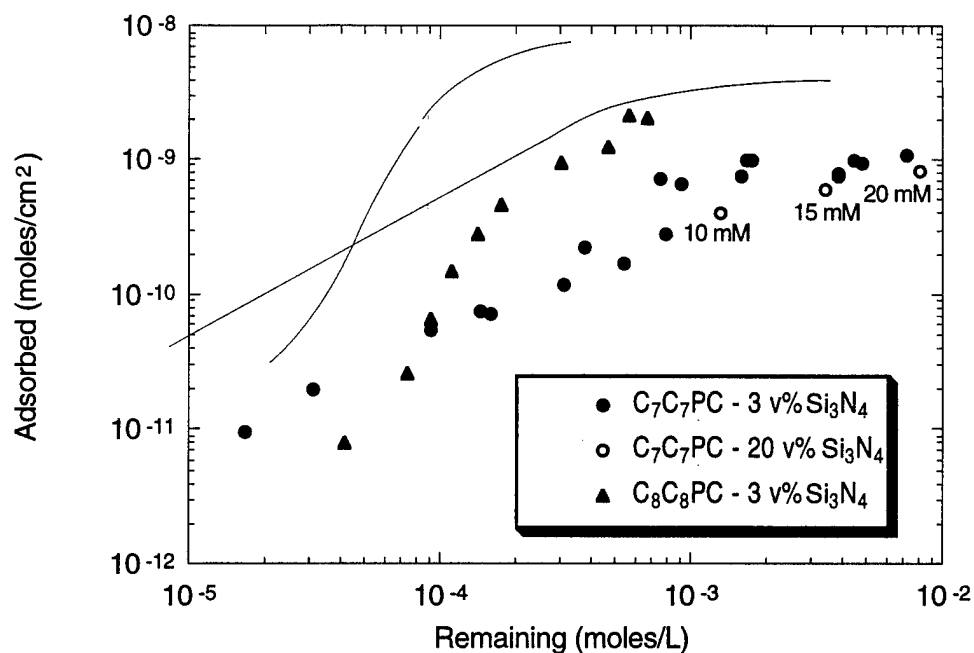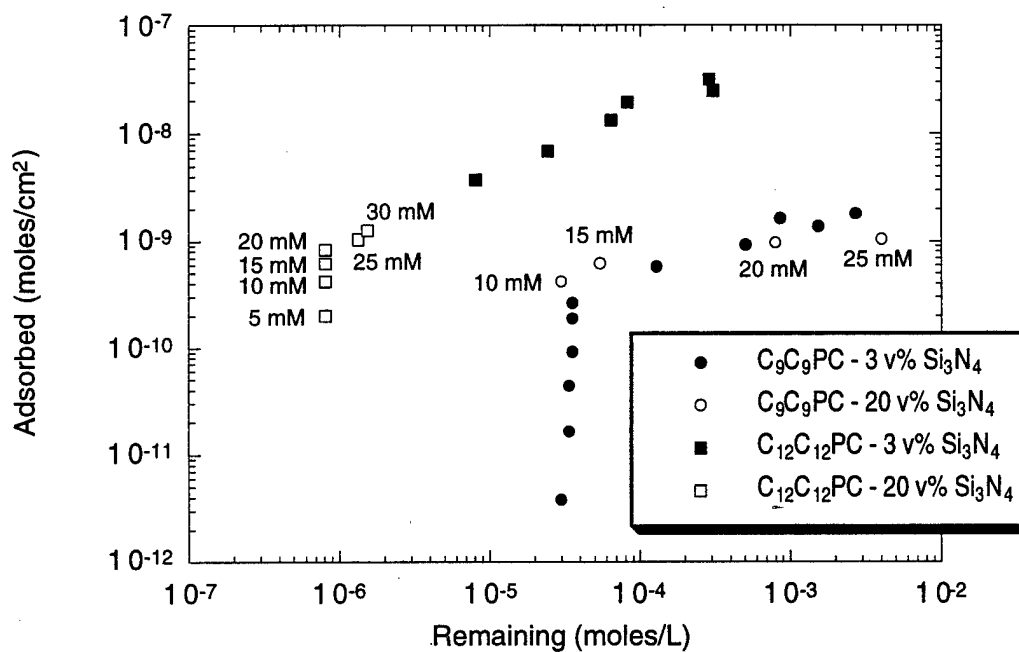
Figure 3 The adsorption isotherms of a 3 vol% silicon nitride suspension at pH 6 with C_7C_7PC (1,2-diheptanoic-sn-glycero-3-phosphocholine) and C_8C_8PC (1,2-dioctanoic-sn-glycero-3-phosphocholine added. The open circles indicate data for a 20 vol% slurry. (Lines are added to guide the eye.)

Figure 4 The adsorption isotherm of a 3 vol% silicon nitride suspension at pH 6 with C_9C_9PC (1,2-dinonanoic-sn-glycero-3-phosphocholine) and C12C12PC (1,2-didodecanoic-sn-glycero-3-phosphocholine) added. The open data points indicate measurements for a 20 vol% slurry.
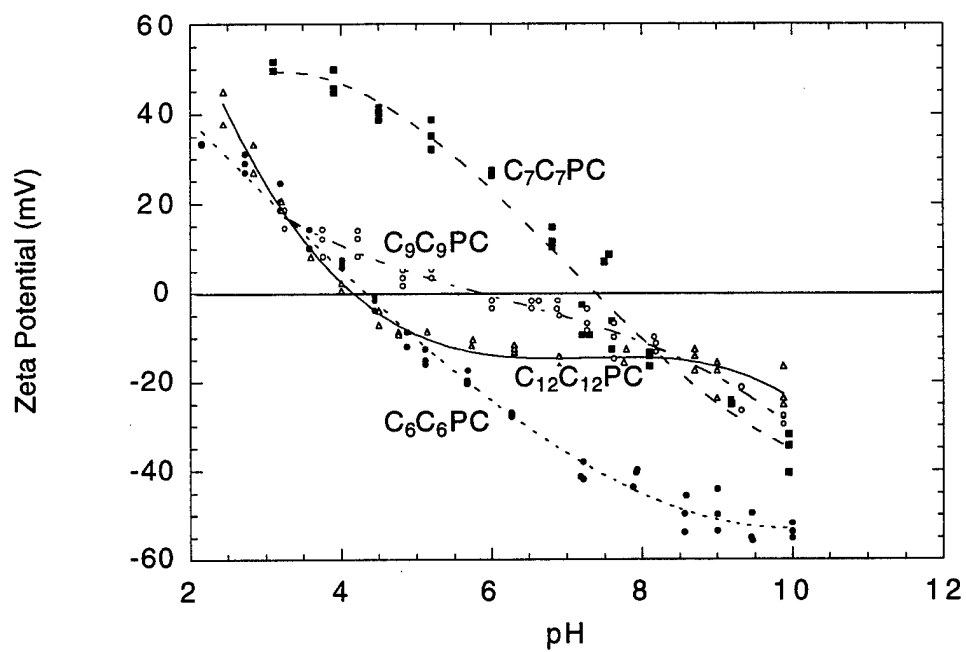
Figure 5 The effect of phosphocholines of different chain lengths on the zeta potential of silicon nitride.
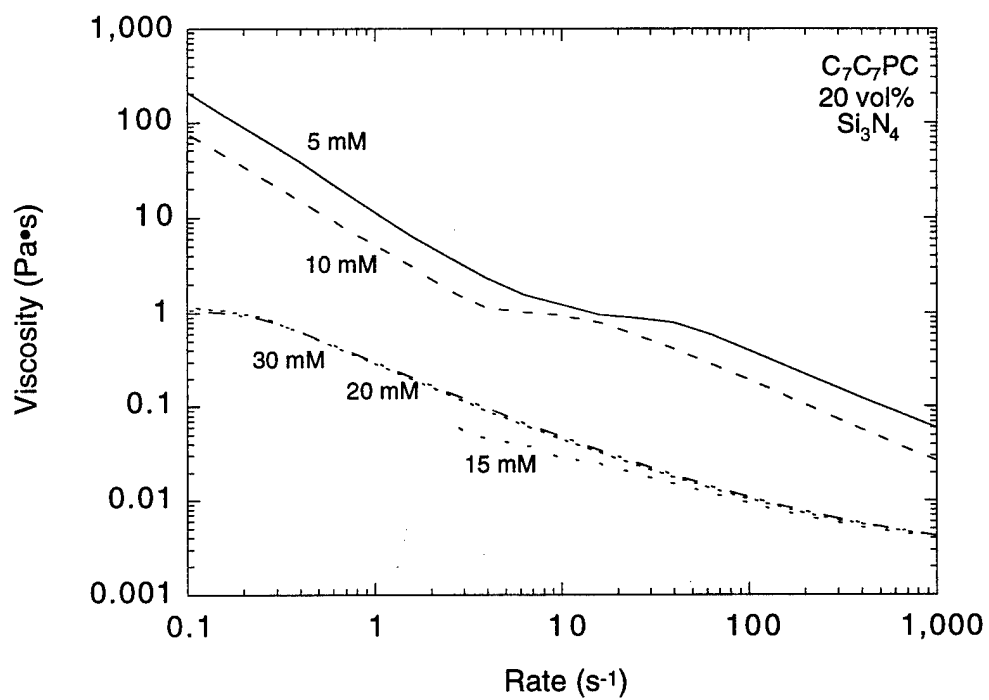
Figure 6 The rheology of silicon nitride slurries (20 vol%) with added C$_7$C$_7$PC (1,2-diheptanoic-sn-glycero-3-phosphocholine) at pH 6.
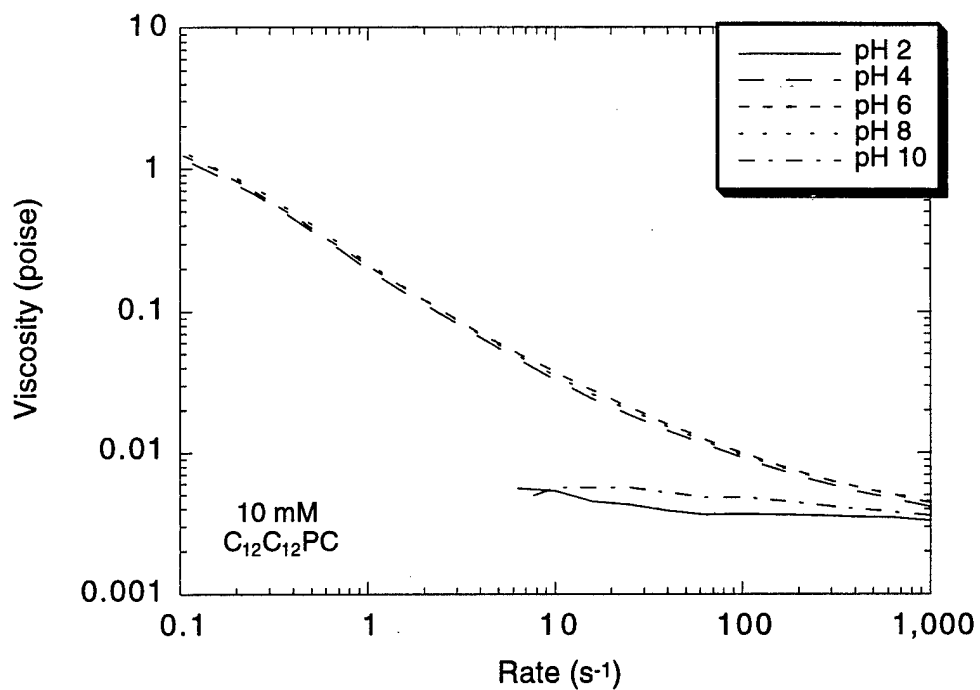
Figure 7 The rheology of silicon nitride slurries (20 vol%) with added $C_{12}C_{12}PC$ (1,2-didodecanoic-sn-glycero-3-phosphocholine) as a function of pH.
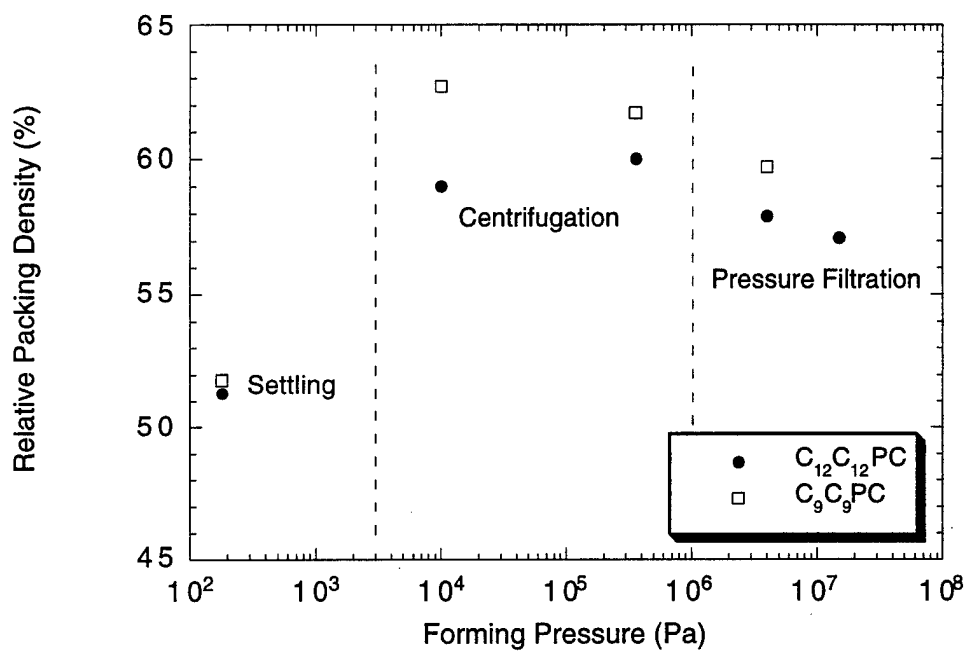
Figure 8 The effect of forming pressure on the packing density of silicon nitride slurries (20 vol%) with added phosphocholine.

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