

The surface chemistry of silicon nitride powder in the presence of dissolved ions

V. A. HACKLEY, S. G. MALGHAN

Ceramics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

Colloidal processing of silicon nitride (Si_3N_4) powders depends largely on the control of reactions at the solid–solution interface. The role of dissolved ions in the surface chemistry of Si_3N_4 powders has been investigated, and the implications of these results for the effects of impurities, contaminants and additives in processing are discussed. The interaction of ions at the solid–solution interface was characterized by particle electrokinetic behaviour determined from electroacoustic measurements in moderately concentrated suspensions. Ions were classified according to chemical similarity and surface specificity. Specific adsorption was inferred from the movement of the isoelectric point relative to the endemic “native” value. Most simple univalent electrolytes behaved indifferently towards the Si_3N_4 surface, with the exception of fluoride which specifically adsorbed and may have formed a strong complex with surface silicon sites. The alkaline-earth cations exhibited a similar weak specificity. In the presence of hydrolysable transition metal cations, powder surface chemistry was controlled by the adsorption of hydroxy metal complexes and by the solubility of a surface-precipitated metal hydroxide phase. Oxo anions, such as sulphate and carbonate, adsorbed specifically on the Si_3N_4 surface, but the interactions were weaker than previously observed on metal oxide surfaces.

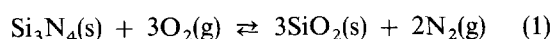
1. Introduction

Stability and rheology of fine-powder slurries is controlled by the chemistry of the solid–solution interface. The interfacial electrochemical properties can be significantly affected by the presence of surface impurities or secondary components added to the suspension. For non-oxide materials, such as silicon nitride, the presence of oxygen in the surface region is known to drastically modify the electrical double-layer properties in a predictable manner. Electrokinetic measurements show that the isoelectric point (i.e.p.) of Si_3N_4 decreases linearly with increasing surface oxide thickness [1, 2]. The concentration of oxygen in the surface layer varies widely between manufacturers, but can be reduced by relatively mild surface treatments [2].

Besides oxygen, commercial Si_3N_4 powders contain varying amounts of additional impurities. Typical bulk concentrations of some common impurities are listed in Table I. The values reported here are taken from data for 21 powders having a surface area greater than $6\text{ m}^2\text{ g}^{-1}$, and represent a cross-section of sources and synthesis routes. Other than oxygen and carbon, the most common elemental impurities are metals, namely magnesium, calcium, aluminium and iron. Many of the elements listed in Table I are known to affect sintered microstructure and high-temperature ceramic strength, however, their possible role in powder surface chemistry and processing is not clear.

In most cases, slips contain one or more secondary components which are added during slurry preparation. These additives are often surface active and may possess acid–base properties. Oxides (e.g. Al_2O_3 , Y_2O_3 , MgO) are usually added as a colloidal phase to the Si_3N_4 suspension. These materials form an oxynitride glass at the Si_3N_4 grain boundary and promote liquid–phase sintering during densification [3]. Incompatible surface chemistry of the constituent solid phases can cause heterocoagulation which leads to phase heterogeneity and poor slip rheology. Sintering aids can also be coated directly onto the Si_3N_4 particle surface using *in situ* heterogeneous precipitation [4] or alkoxide condensation reactions [5]. Organic polymers are routinely added to slips to control particle dispersion and green body strength. Polyelectrolyte dispersants, for example, provide additional stability through electrosteric repulsive forces and interact strongly with surface sites on Si_3N_4 [6].

The surface structure of Si_3N_4 , shown schematically in Fig. 1, is composed of acidic silanol ($\text{Si}-\text{OH}$) and basic silazane ($\text{Si}_2=\text{NH}$) groups [7]. The relative abundance of these sites varies with the surface oxide content [8]. A silica-rich surface layer can result from oxidation of the thermodynamically unstable Si_3N_4 surface according to Equation 1 [9, 10].



Previous studies have also shown that hydrolysis of

TABLE I Average concentration and range of common impurities found in commercial silicon nitride fine powders

	Chemical composition of impurities by element									
	O (%)	C (%)	Al (ppm)	Fe (ppm)	Ca (ppm)	Mg (ppm)	Cr ^a (ppm)	Cu ^a (ppm)	Na ^a (ppm)	Cl ^b (ppm)
Average	1.4	0.23	670	470	310	110	4	3	2	50
High	2.5	0.9	2000	2100	2000	400	—	—	—	—
Low	0.4	0.1	10	16	2	2	—	—	—	—

^a Only two values available for averaging. ^b Value for single powder produced by reaction of SiCl₄ + NH₃ (used in present study).

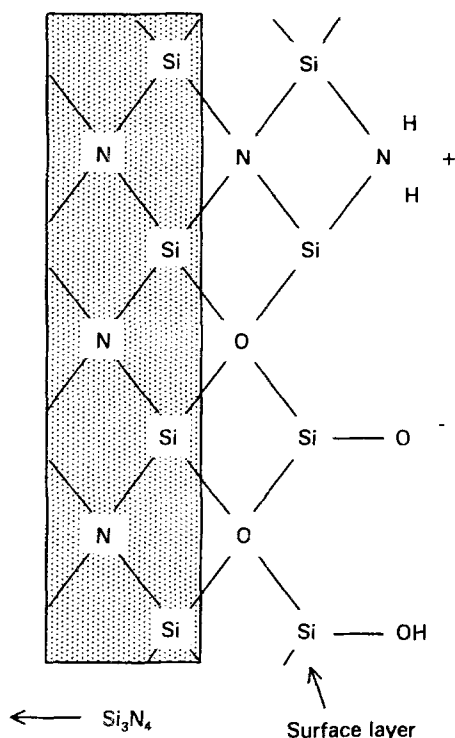
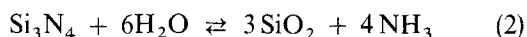


Figure 1 Schematic depiction of hydrolysed Si₃N₄ surface structure.

Si₃N₄ to silica and ammonia can occur readily at room temperature [9, 11]



As the oxide content of the surface layer increases, the Si-OH site density increases proportionately and the surface becomes more acidic. In aqueous solution, Si-OH and Si₂=NH sites generate surface charge by the adsorption of potential determining OH⁻ and H⁺ ions. Surface sites may also form complexes with dissolved ionic species. The resulting electrical properties of the dispersed particles will determine their interaction with each other and with other charged species in suspension.

In this paper the electrokinetic properties of Si₃N₄ suspensions in the presence of various ionic species, with the purpose of describing the electrostatic component of these interactions as a function of pH, have been examined. An electroacoustic technique was used to determine the particle electrophoretic mobility in

moderately concentrated suspensions. Ionic species were chosen based on their importance as impurities or additives, and to represent a cross-section of chemical reactivities. Organic additives are not treated in the present work, but will be addressed separately in a future publication.

2. Experimental procedure

The model powder chosen for this study was Ube Industries (Japan) SNE-10[†] (Lot no. A910732). This was a high-purity Si₃N₄ powder with a BET surface area and mean particle diameter measured at 10.1 ± 0.2 m² g⁻¹ and 0.40 ± 0.01 μm, respectively (uncertainty expressed as estimated standard deviation determined from a series of independent observations). Particle size was determined after ultrasonic dispersion using a light diffraction technique (LA900, Horiba, Irvine, CA). The bulk powder composition as obtained from the manufacturer is given in Table II.

All acids, bases and salts used were of reagent grade or better. Standard low-carbonate sodium hydroxide titrants (EM Science, Gibbstown, NJ) were used in all experiments.

Suspensions (2 vol %) were prepared for analysis by adding 15.9 g of powder to an appropriate amount of deionized water containing electrolyte. Nitric acid was used to adjust the final pH to between 2 and 3.8, depending on the experiment. The suspension was ultrasonicated using a probe at 40 W output power for a total time of 9 min in 3 min cycles. The suspension

TABLE II Composition of model powder^a

Component	Concentration
N (wt %)	> 38.0
O (wt %)	1.29
C (wt %)	< 0.2
Al (ppm)	< 100
Fe (ppm)	< 50
Ca (ppm)	< 50
Cl (ppm)	< 100
Crystallinity (wt %)	> 99.5
α-phase (wt %)	> 95

^a Manufacturer specifications; % Si by difference.

[†] Certain trade names and company products are mentioned in the text or identified in illustrations in order to adequately specify the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.

was cooled using an ice-bath between treatments. In the case of multivalent ions (except the alkaline-earths) the electrolyte was added after sonication. In the case of some hydrolysable metal cations (Fe^{III}, Al^{III}, Cr^{III} and Cu^{II}) the initial pH of the suspension was between 2 and 3, while the electrolyte solution pH was between 1 and 3. All electrolyte solutions were prepared fresh for each set of experiments. Unless specifically noted, electrolyte concentrations were fixed at 0.01 equivalents l⁻¹ (eq l⁻¹) based on the indicated valence for a specified ion. For example, 0.005 mol l⁻¹ for a metal ion M²⁺ or M^{II} was equivalent to 0.01 eq l⁻¹. This was done for comparative purposes and may not represent the actual ionic state over the entire titration pH range.

Suspensions were placed in a 300 cm³ Teflon cell attached to the electroacoustic analysis system (ESA 8000, Matec Applied Sciences, Hopkinton, MA), equipped with an autotitrator, overhead stirrer and probes for pH, temperature and conductivity. Titrations were performed at 20 ± 1°C under a blanket of nitrogen gas with continuous stirring. Suspension pH and electroacoustic measurements were recorded at 60 s intervals following each titrant addition. During the analysis a high frequency (~ 1 MHz) electric field was applied to the suspension which generated a sound wave at the electrode surface. The pressure amplitude of this wave, termed the electrokinetic sonic amplitude (e.s.a.), and the phase angle relative to a standard of known polarity were measured. For moderately concentrated suspensions (up to 10%) the e.s.a. signal is proportional to the difference in density between the solid and liquid phases, ($\Delta\rho$), the solids volume fraction, (ϕ), and the dynamic or frequency-dependent electrophoretic mobility of the particles, $\mu(\omega)$ [12]. The dynamic mobility is approximately equivalent to the static field electrophoretic mobility under the conditions of the present experiments, and therefore is related in the same manner to the shear-plane or zeta potential of the particles. A detailed description of this technique and its application to ceramic powders may be found elsewhere [2, 12–14]

3. Results and discussion

3.1. Electrical double-layer

When a powder is dispersed in water an electrical charge is formed at the solid–liquid interface due to the adsorption of potential determining ions. The net charge and potential of the particle depend on the relative density of positive and negative surface sites. For Si₃N₄ this is determined primarily by surface oxygen content and suspension pH [1, 2, 8]. The surface charge is balanced by an accumulation of counter-ions in the surrounding liquid, thereby forming an electrical double-layer (Fig. 2). The charge distribution in the liquid can be divided into two regions: 1. a *compact layer* close to the particle surface where potential determining ions adsorb and chemical interactions occur; and 2. a *diffuse layer* extending out to the bulk solution in which purely electrostatic effects are observed. This simple but functional description of the double-layer, the Gouy–

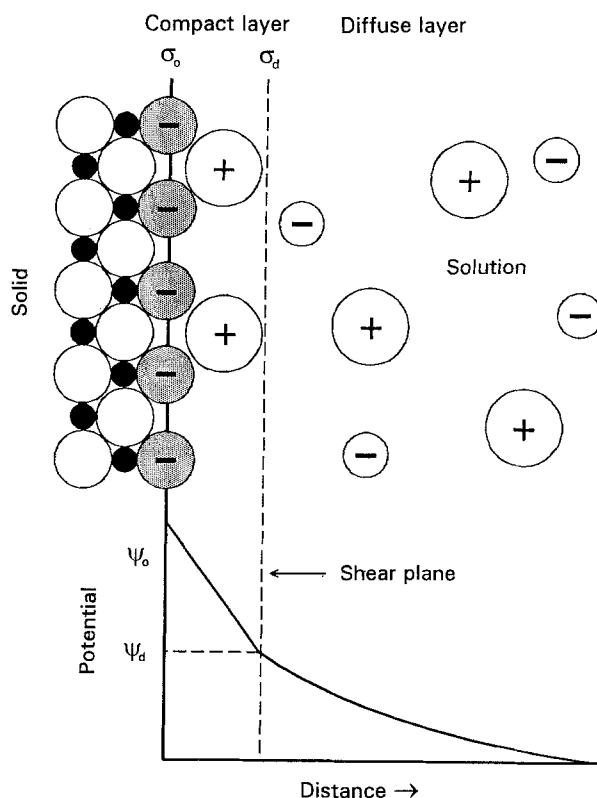


Figure 2 Gouy–Chapman–Stern model of the electrical double-layer and potential decay at an oxide–water interface: ○, lattice oxygen; ⊙, surface oxygen; ●, metal ion; ⊕ ⊖, solution ions.

Chapman–Stern model [15], incorporates the principal elements required to interpret the present work.

The shear-plane indicated in Fig. 2 defines the hydrodynamic boundary of the particle and is characterized by the electrokinetic or zeta potential. In an applied electric field the particle, solution and associated charge contained within this hydrodynamic boundary moves as a single unit. The electrophoretic mobility, or particle velocity per unit applied field strength, characterizes the total diffuse layer charge and is sensitive to changes occurring on the surface or in the compact layer. Evidence indicates the shear-plane is located very near to the outer surface of the compact layer, and therefore relatively close to the particle surface [15]. The i.e.p. is defined as the pH at which the electrophoretic mobility (zeta potential) is zero and the electrokinetic charge changes sign. This condition is often referred to as a particle charge reversal, however this is a somewhat ambiguous statement since technically the i.e.p. represents the electrokinetic (diffuse layer) charge and not the particle surface charge.

3.2. Simple univalent electrolytes

The primary effect that simple ions have on charged particles is compression of the double-layer. This effect is manifested through the Debye–Hückel parameter, κ [15]:

$$\kappa = \left(\frac{e^2 \sum n_i z_i^2}{\epsilon k T} \right)^{1/2} = 3.29 l^{1/2} (\text{nm})^{-1} (\text{at } 25^\circ\text{C in water}) \quad (3)$$

where e is the electron charge, n_i the ion concentration of the i th ion, z_i the ion valance, ϵ the dielectric constant, k the Boltzmann constant, T the temperature and I the ionic strength. The reciprocal Debye–Hückel parameter, $1/\kappa$, has units of length, and is a measure of the double-layer thickness. As the ion concentration increases, the surface charge is screened and the electrical potential decreases more rapidly at an increasing distance from the surface. The balance of charge on the surface is unaffected by these ions, and therefore the i.e.p. is constant.

Sodium nitrate illustrates this type of behaviour for Si_3N_4 . In Fig. 3 $\mu(\omega)$ is shown as a function of pH and NaNO_3 concentration. The curves cross the zero mobility line at a common intersection point (c.i.p.) at pH 6.4. The c.i.p. may be identified as the “native” i.e.p. for this powder, and serves as a basis for comparison of other ions. Sodium nitrate is a convenient background electrolyte for electroacoustic measurements in general, because it makes a relatively small contribution to the sonic amplitude signal and phase shift. Some electrolytes generate a significant electro-

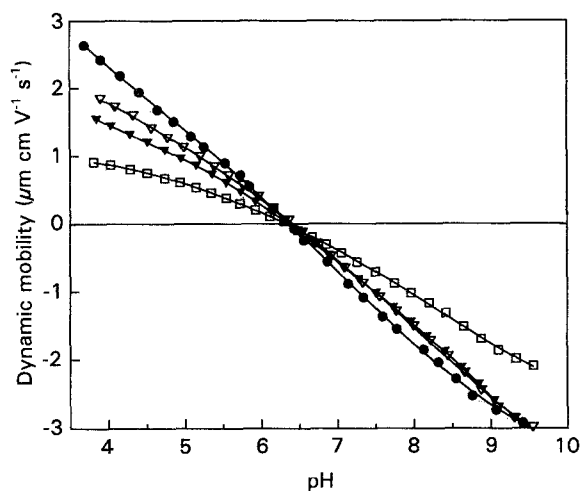


Figure 3 Electrokinetic titration curves for Si_3N_4 in NaNO_3 solutions as a function of electrolyte concentration: ●, no electrolyte; ▽, $0.0025 \text{ mol l}^{-1} \text{ NaNO}_3$; ▼, $0.01 \text{ mol l}^{-1} \text{ NaNO}_3$; □, $0.05 \text{ mol l}^{-1} \text{ NaNO}_3$.

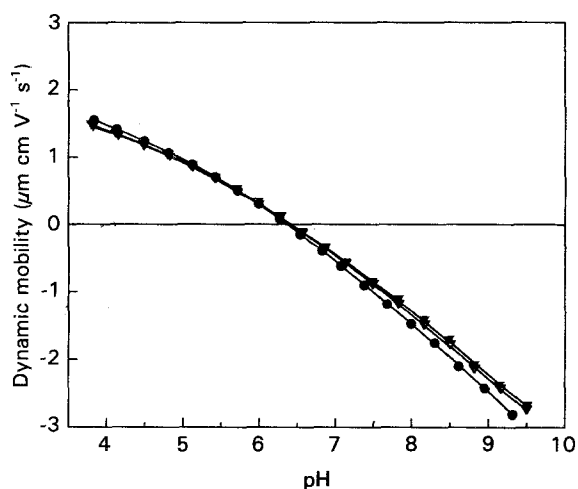


Figure 4 Electrokinetic titration curves for Si_3N_4 in 0.01 mol l^{-1} electrolyte solutions. ●, NH_4NO_3 ; ▽, NaCl ; ▼, KNO_3 .

acoustic signal which can cause artifacts such as a false i.e.p. shift [13, 16]. A blank subtraction method can be used to remove this background signal.

Fig. 4 shows titration curves for Si_3N_4 in the presence of three simple 1:1 electrolytes (NH_4NO_3 , NaCl and KNO_3). Each curve yielded an i.e.p. of 6.4, and therefore these ions can be classified as indifferent. This is particularly significant in the case of NH_4NO_3 , since ammonia is a ubiquitous component in Si_3N_4 processing. It is standard practice to use NH_4OH to adjust pH in slurries, due to the detrimental effects of alkali metals on grain boundary composition. Additionally, NH_3 is associated with the surface as a result of the reaction shown in Equation 2. The odour of ammonia is often evident with a freshly opened container of Si_3N_4 powder. The suspension can continue to release ammonia into solution even after 24 h [2]. Any interaction of ammonia with the Si_3N_4 surface is apparently physical in nature, however, since the presence of this species does not alter the surface chemistry.

Any ion with a non-electrostatic adsorption energy contribution can be regarded as specifically adsorbed. Within this rather broad grouping, a further division can be made between those ions that adsorb chemically (sharing of electrons) and those that do not. For chemical interaction to occur the ion must penetrate the compact layer. Experimentally, a chemical interaction with the surface is evidenced by superequivalent adsorption, reversal of the zeta potential sign or by a shift in the i.e.p. [17]. The adsorption of cations will cause a positive (alkaline) shift in the i.e.p., while anions will cause a negative (acidic) shift. This effect is due to the accumulation of excess positive or negative charge in the compact layer, which, to obtain charge neutrality at the i.e.p., must be compensated for by the additional uptake of OH^- or H^+ potential determining ions, respectively. A lyotropic sequence, on the other hand, is preferential adsorption within a grouping of ions that results from differences in ion size or shape (including the hydration shell), and therefore does not affect the i.e.p. (i.e. specific but not chemical).

The $\mu(\omega)$ -pH curves for Si_3N_4 in a series of potassium halide solutions are presented in Fig. 5. The

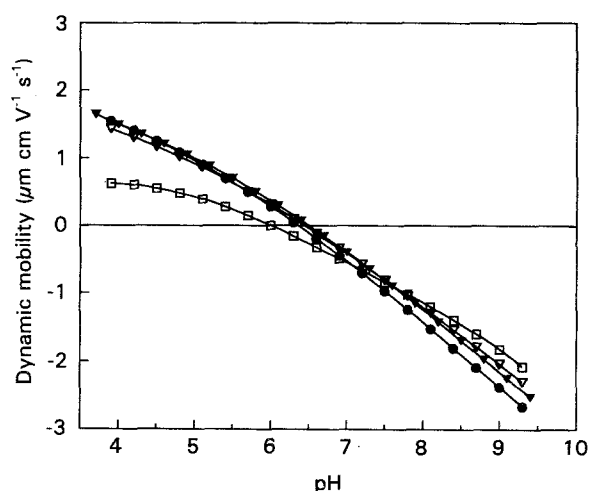


Figure 5 Electrokinetic titration curves for Si_3N_4 in 0.01 mol l^{-1} potassium halide solutions. ●, KI ; ▽, KBr ; ▼, KCl ; □, KF .

salts of I^- , Br^- and Cl^- yields the native i.e.p. of 6.4, and are therefore indifferent. In the case of F^- the i.e.p. was shifted to pH 6 and the positive mobility maximum is significantly reduced. This behaviour is indicative of specific adsorption.

The small size of the weakly hydrated fluoride ion enables it to penetrate the compact layer and interact with the surface. Fluoride, a ligand, may then complex the positively charged surface $Si_2=NH_2^+$ groups. Additionally, F^- can be expected to exchange with OH^- in surface silanols to form a stable monodentate complex with this group [18, 19]. These reactions have important consequences for processing. Fluorine is found as a surface impurity in some Si_3N_4 powders produced by carbothermal reduction and subsequently treated with HF to remove residual SiO_2 [2]. The fact that F^- forms relatively strong complexes with the Si_3N_4 surface suggests that this species may be difficult to remove from powders. Halides have been implicated in the high-temperature strength reduction of liquid-phase sintered Si_3N_4 [20].

3.3. Alkaline-earth cations

As seen in Table I, alkaline-earth metals are among the major impurities commonly found in commercial Si_3N_4 powders. In their ionic form these elements are divalent and readily form stable oxides and carbonates. Alkaline-earth oxides, such as MgO, are used as sintering aids. The glassy phase formed from these oxides during sintering, however, is characterized by a lower softening point, relative to some transition metal oxides [21]. The presence of alkaline-earths in the starting powders is probably not as detrimental to sintering as the presence of halides, but may still contribute to reduced ceramic strength if grain boundary segregation occurs.

Titration curves for Si_3N_4 in the presence of 0.005 mol l^{-1} (0.01 eq l^{-1}) nitrate salts of Mg^{II} , Ca^{II} and Ba^{II} are shown in Fig. 6, relative to the curve for $NaNO_3$. The i.e.p. is shifted to about pH 6.9 in each

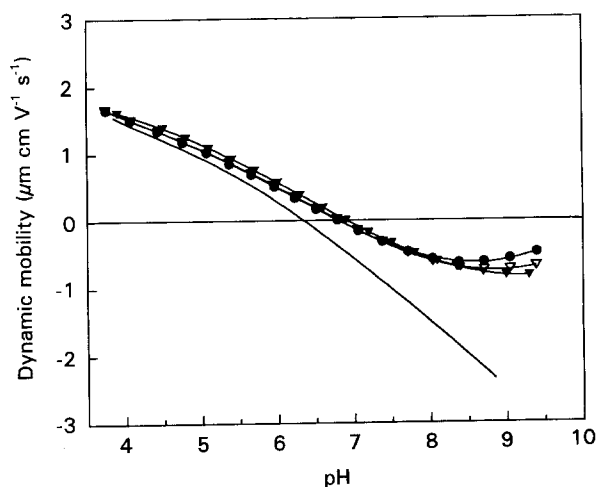


Figure 6 Electrokinetic titration curves for Si_3N_4 in 0.005 mol l^{-1} alkaline-earth nitrate solutions compared to 0.01 mol l^{-1} $NaNO_3$ solution. ●, $Mg(NO_3)_2$; ▽, $Ca(NO_3)_2$; ▼, $Ba(NO_3)_2$; — $NaNO_3$.

case, while the negative mobility is greatly reduced. The downward (acidic) i.e.p. shift indicates specific adsorption of the metal cations, but the data do not show significant differences in affinity. The cations were most likely interacting with $Si-OH$ surface sites, and based on this assumption it is not surprising to find virtually identical i.e.p.s for the three ions. Dugger *et al.* [22] determined the free energy of formation for the metal-silanol complex under acidic conditions and found similar values for Mg, Ca and Ba (-1.1 , -1.5 and $-1.5 \text{ kcal per metal surface bond}$, respectively). In agreement with these findings, Tadros and Lyklema [23], using surface charge measurements, found that below pH 7.5 the alkaline-earth ions behaved similarly and interacted weakly with the surface. Above pH 7.5, however, they found that the negative surface charge decreased in the lyotropic sequence $Ba > Ca > Mg$ (i.e. decreasing ion size). The mobility data in Fig. 6 is not definitive, but it indicates an increase in surface affinity above pH 7.5 that follows the same sequence found by Tadros and Lyklema [23]. This interpretation is based on the decrease in negative mobility. These results suggest that Si_3N_4 essentially has the same cation adsorption properties as SiO_2 , and that the $Si_2=NH$ groups do not significantly participate in these reactions.

The sequential affinity of these ions in alkaline solution may be associated with the adsorption of hydroxy complexes, as suggested by Fuerstanau and Palmer [24]. The selectivity may be explained by the following line of reasoning. Charge density increases with decreasing ion size in the series, resulting in greater hydration and a stronger tendency to hydrolyse [25]. Hydroxy complexes are highly surface active and bind more strongly with surface silanols than the hydrated metal ion. This effect becomes pronounced for the more easily hydrolysed transition metals.

3.4. Hydrolysable metal cations

This group includes the polyvalent cations of the transition and *p*-block metals which readily hydrolyse and tend to precipitate solid hydroxides and oxides. Below the precipitation concentration these ions form a variety of mono- and polynuclear hydroxy complexes, the distribution of which depends primarily on solution pH.

An important application of the interactions discussed below concerns the use of metal oxide sintering aids such as Y_2O_3 , Al_2O_3 , CeO_2 , La_2O_3 and ZrO_2 [3]. These materials are typically added to Si_3N_4 slips as a secondary particulate phase and then mechanically mixed to obtain a homogeneous distribution. The surface chemistry of the dispersed components are often incompatible at the processing pH, and ultimately lead to problems of heterocoagulation, segregation and undesirable reactions with dispersants and binders. In order to alleviate these problems, chemical methods of sintering aid addition have sometimes been utilized. These methods generally involve reaction of a metal salt [4, 5] or alkoxide [26] with the Si_3N_4 surface to form an oxide/hydroxide coating,

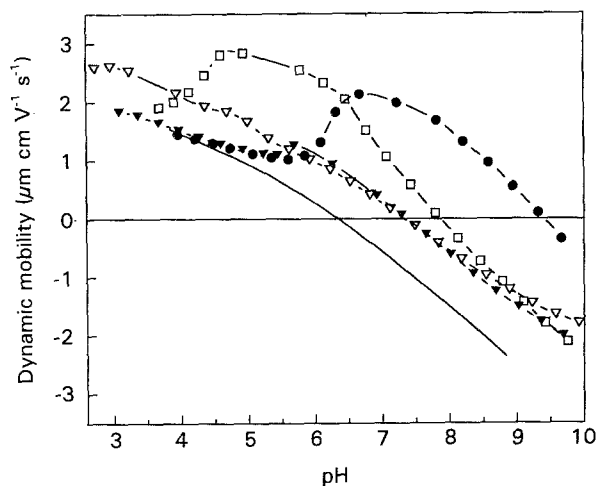


Figure 7 Electrokinetic titration curves for Si_3N_4 in metal nitrate solutions compared to $0.01 \text{ mol l}^{-1} \text{ NaNO}_3$ (—): $0.005 \text{ mol l}^{-1} \text{ Cu(II)}$ (●); $0.0033 \text{ mol l}^{-1} \text{ Fe(III)}$ (▽), Cr(III) (▼) and Al(III) (□).

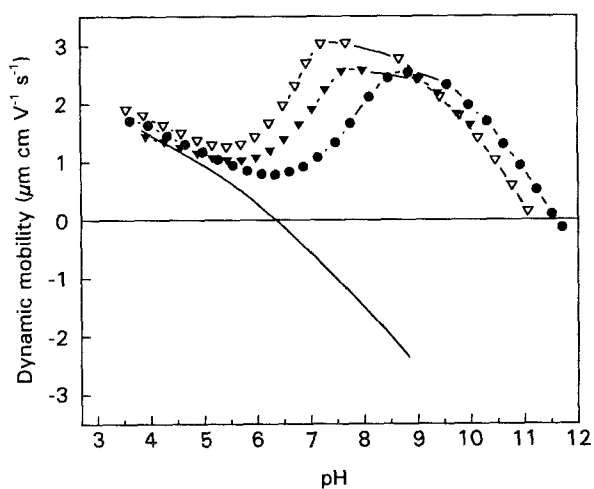
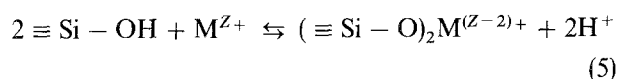
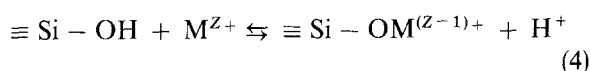


Figure 8 Electrokinetic titration curves for Si_3N_4 in $0.0033 \text{ mol l}^{-1}$ rare-earth nitrate solutions [Er(III) , ▽; Y(III) , ▼; La(III) , ●] and $0.01 \text{ mol l}^{-1} \text{ NaNO}_3$ solution (—).

thereby incorporating the sintering aid(s) into the substrate and generating both a homogeneous distribution and a uniform surface chemistry. In order to adequately control sintering aid deposition and slip properties it is necessary to understand the complexation–hydrolysis–precipitation relationships involved.

Electroacoustic titrations of Si_3N_4 in the presence of Cu^{II} , Fe^{III} , Cr^{III} and Al^{III} nitrate solutions (Fig. 7) and Er^{III} , Y^{III} and La^{III} nitrate solutions (Fig. 8) exhibit a distinctly different behaviour than that observed for the alkali and alkaline-earth metal ions. The appearance of a maximum followed by a relatively large shift in the i.e.p. indicates a stronger and more complex interaction between the dissolved ion and particle surface over this pH range. Adsorption of the free metal ion and hydroxy complex at the Si_3N_4 –solution interface below pH 9 (the approximate $\text{p}K_a$ for $\text{Si}_2=\text{NH}_2^+$ [8] would presumably be dominated by

reaction at the weakly acidic $\text{Si}-\text{OH}$ sites. Previous studies [19, 27] have suggested that surface $\text{Si}-\text{OH}$ groups form monodentate and bidentate complexes with polyvalent metal ions:



At more alkaline pH values, $\text{Si}_2=\text{NH}$ sites may come involved in complexation or hydrogen bonding of metal ions.

Similarities exist between the electrokinetic behaviour observed for Si_3N_4 in the presence of hydrolysable metal cations and that of oxide systems [24, 28]. The specific mechanisms responsible for this behaviour have been widely debated and are variably attributed to: 1. adsorption of the free cation; 2. adsorption of the mononuclear hydroxy complex; 3. adsorption of a polynuclear hydroxy complex; 4. heterogeneous precipitation of hydroxide on the substrate surface. It is likely that all or several of these mechanisms are operable in a given system, depending on metal ion concentration, pH, ionic strength and particle surface area. James and Healy [28] showed that up to three reversals of the electrokinetic potential (i.e.p.s) could occur when polyvalent metal ions were present during the acid–base titration of oxides. The authors attributed these “charge” reversals, in order of increasing pH, to the native substrate (CR1), the onset of surface hydroxide precipitation (CR2) and the mixed substrate/precipitate surface (CR3). The last reversal (CR3) approached the i.e.p. of the pure hydroxide precipitate as surface coverage of the substrate was completed. In other words, as pH and metal ion

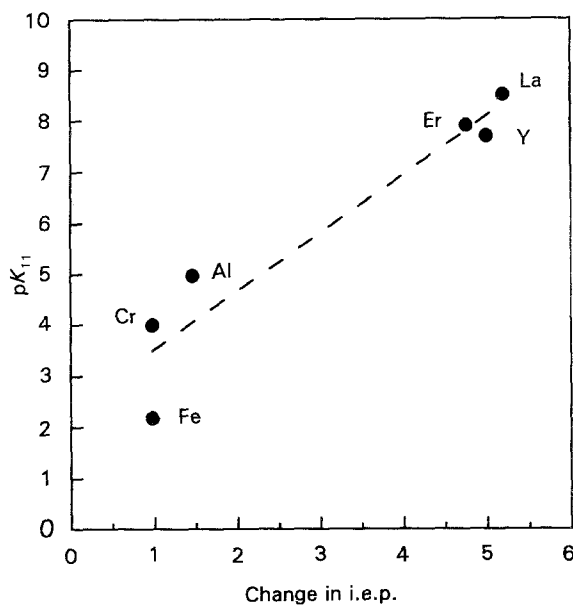


Figure 9 Correlation between the formation constant for the first hydrolysis product (K_{11}) and the isoelectric point (i.e.p.) shift of Si_3N_4 measured in the presence of $0.0033 \text{ mol l}^{-1}$ metal nitrate solution.

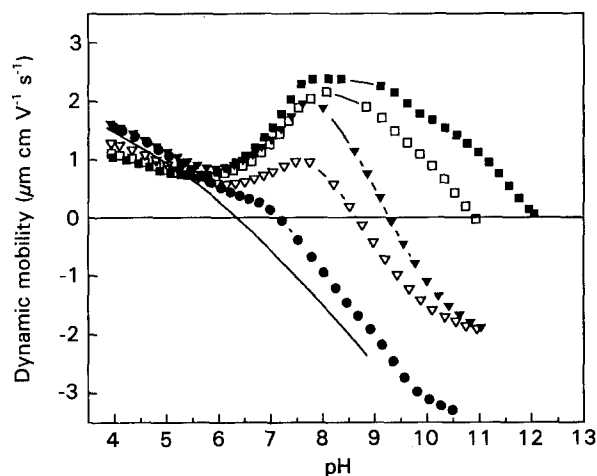


Figure 10 Electrokinetic titration curves for Si_3N_4 in 0.01 mol l^{-1} NaNO_3 as a function of added $\text{Y}(\text{NO}_3)_3$ concentration [mol l^{-1}]: ■, 0.005; □, 0.0025; ▼, 0.001; ▽, 0.0005; ●, 0.0001; —, 0].

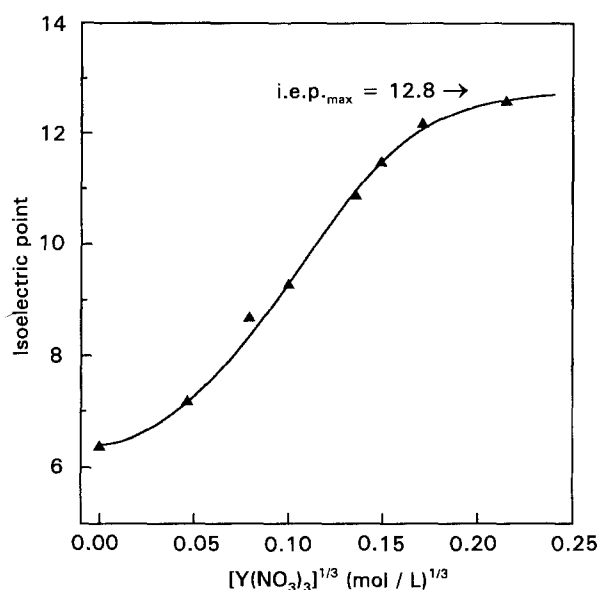


Figure 11 The isoelectric point (i.e.p.) of Si_3N_4 as a function of $\text{Y}(\text{NO}_3)_3$ concentration, showing the predicted asymptotic maximum value for the isoelectric point.

concentration increased, control of surface chemistry switched from adsorption to precipitation, and eventually the Si_3N_4 particles exhibited the acid–base properties of the secondary hydroxide phase.

The electrokinetic behaviour of Si_3N_4 (or any substrate) in the presence of polyvalent metal ions is intimately tied to the hydrolysis properties of the ion and the solubility and acid–base properties of the hydroxide precipitate. For oxides and hydroxides, the latter two properties are closely related; the pH of minimal solubility and the zero point of charge or i.e.p. are coincident [29]. These relationships are clearly demonstrated for Si_3N_4 in Figs 9–11. The formation constant (K_{11}) for the first hydrolysis product (Equation 6) characterizes the tendency for a metal ion to hydrolyse and is generally the first stage prior to

precipitation of the hydroxide.



Fig. 9 shows the correlation between $\text{p}K_{11}$ [values from ref. 25] and the degree to which the i.e.p. is shifted relative to the native i.e.p. at a constant metal ion concentration. Clearly, the i.e.p., which may be identified with CR3 according to the terminology of James and Healy [28], increases with decreasing tendency of the metal ion to hydrolyse. In other words, as the solubility in acidic solution of the corresponding hydroxide precipitate increases, the i.e.p. has to increase toward more alkaline pH values. In this context, it should be noted that Mg^{II} , Ca^{II} and Ba^{II} may undergo similar hydrolysis–precipitation reactions with Si_3N_4 , but because the $\text{p}K_{11}$ values for these ions is above 11 (see Fig. 9) the precipitation pH will be shifted to more basic values relative to the species in Figs 7 and 8. This is in fact the case as reported by Fuerstenau and Palmer [24] for Mg^{II} on SiO_2 , which showed CR2 occurring around pH 10. The nonconformity shown by Fe^{III} in Fig. 9 may be due to colloidal iron hydroxide or oxyhydroxide which could be present in the nitrate solution prior to titration. The hydrolysis of Fe^{III} begins ca. pH 1, and it is therefore difficult to avoid premature homogeneous precipitation in moderately concentrated electrolyte solutions.

A similar relationship exists between the solubility product for the metal hydroxide and the mixed substrate–precipitate i.e.p. This correlation is not reported because there is greater uncertainty associated with the determination and selection of an appropriate solubility product to represent the surface-precipitated phase.

An examination of the Y^{III} concentration dependence of the i.e.p. shift offers further insight into this phenomenon. Yttrium is generally grouped with the lanthanides because of similar hydrolysis and chemical behaviour. Fig. 10 shows a series of titration curves for Si_3N_4 as a function of increasing concentration of $\text{Y}(\text{NO}_3)_3$ in 0.01 mol l^{-1} NaNO_3 solution. The development of the characteristic electrokinetic curve in the presence of hydrolysable metal ions is apparent in this data. The absence of CR2, which was well defined in the concentration series data of James and Healy [28] for Co^{II} and La^{III} on SiO_2 , is due to the close proximity of the native i.e.p. and CR2 in the present case. The apparent i.e.p. or CR3 shifts progressively toward alkaline pH values with increasing Y^{III} concentration, approaching the i.e.p. of the pure hydroxide surface. This is more evident in Fig. 11, where i.e.p. is plotted versus $[\text{Y}^{\text{III}}]^{1/3}$. The data is fitted with a sigmoid function which approaches an asymptotic i.e.p. value of 12.8, representing complete surface coverage of the substrate by the hydroxide precipitate. In addition, titration of a $\text{Y}(\text{OH})_3$ suspension, precipitated from a $\text{Y}(\text{NO}_3)_3$ solution and then washed with deionized water at pH 8 and aged for three days, yielded an extrapolated i.e.p. of 12.8–13.0. The hydroxide-coated Si_3N_4 surface, shown schematically in Fig. 12, behaves electrochemically as if it were a pure $\text{Y}(\text{OH})_3$ phase.

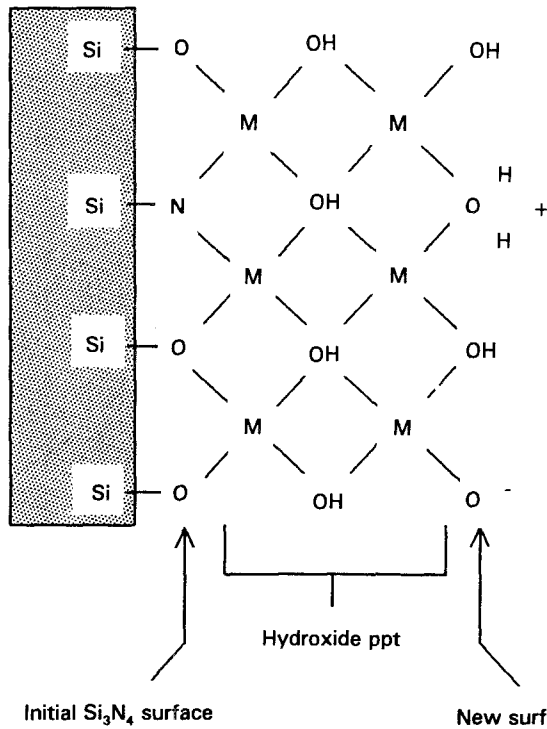


Figure 12 Schematic depiction of the Si_3N_4 -solution interface following heterogeneous precipitation of a metal hydroxide.

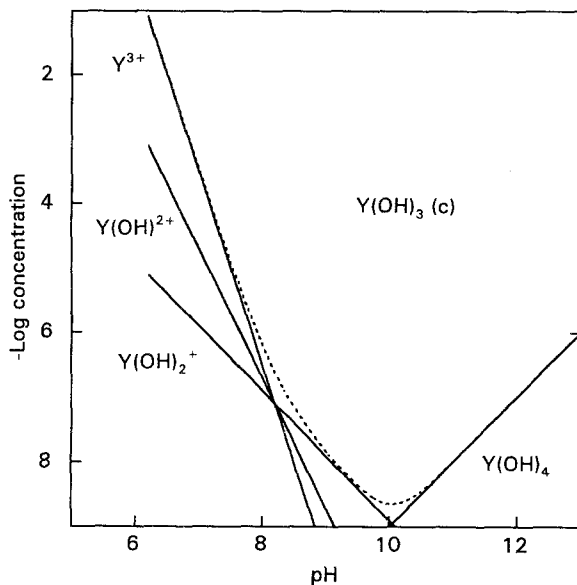
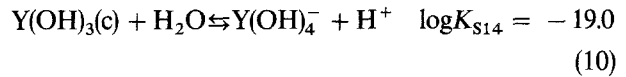
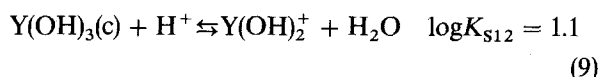
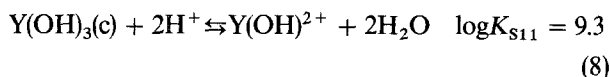
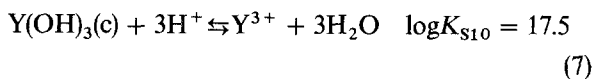


Figure 13 Solubility diagram for Y(III) showing the distribution of soluble species in equilibrium with the solid hydroxide phase as a function of pH.

The solubility of $\text{Y}(\text{OH})_3$ in water can be described by the following set of reactions between the solid and dissolved phases:



The values listed for the solubility constants pertain to a well-aged crystalline precipitate [25], and may not apply to a fresh precipitate of unknown crystallinity and activity. By combining Equations 7–10, a solubility diagram can be constructed (Fig. 13), it shows the distribution of soluble species in equilibrium with the solid phase as a function of pH. Polynuclear species have not been included, partly because precipitation occurs shortly after hydrolysis initiates above pH 6. The inclusion of these species would not greatly affect the equilibrium distribution. The steepness of the solubility boundary (dashed line) in Fig. 13 is indicative of the rapid onset of precipitation above pH 6. The pH of minimal solubility occurs near pH 10 in this diagram. This value occurs significantly lower than the measured i.e.p. of 12.8 for the surface saturated Si_3N_4 -precipitate system and the freshly precipitated $\text{Y}(\text{OH})_3$, and slightly higher than the reported i.e.p. value of 8.95 for hydrous Y_2O_3 precipitated from $\text{Y}(\text{NO}_3)_3$ with NaOH [30]. The more alkaline i.e.p. found in the present case may indicate that the surface precipitated compound is a metastable active or amorphous form.

As a final note on this subject, Si_3N_4 powders vary widely in their pH-surface charge behaviour, primarily as a result of differences in the degree of surface oxidation as mentioned previously. This variation in powder surface properties will significantly impact surface precipitation reactions of metal ions and modify the chemistry of the mixed substrate-precipitate surface.

3.5. Oxo anions

This important group of ions includes sulphate, phosphate, silicate and carbonate, all of which constitute multivalent conjugate bases of oxo acids. The acidity of the oxo acid form decreases in the order H_2SO_4 ($\text{p}K_1 \sim -3$, $\text{p}K_2 = 1.9$) $>$ H_3PO_4 ($\text{p}K_1 = 2.1$, $\text{p}K_2 = 7.2$) $>$ H_2CO_3 ($\text{p}K_1 = 6.3$, $\text{p}K_2 = 10.3$) $>$ $\text{SiO}(\text{OH})_2$ ($\text{p}K_1 \sim 10$). The association of these species with naturally occurring colloidal oxides is critically important in the transport and attenuation of nutrients and pollutants. In the processing of Si_3N_4 these species are not considered primary impurities, however their interactions are of fundamental interest in studying the surface chemistry of this system.

Fig. 14 shows the mobility curves for Si_3N_4 in the presence of 0.005 mol l^{-1} (0.01 eq l^{-1}) K_2HPO_4 , Na_2SiO_3 (metasilicate) and K_2SO_4 , and also $0.0017 \text{ mol l}^{-1}$ (0.01 eq l^{-1}) $(\text{NaPO}_3)_6$ (hexameta-phosphate). All of these species cause an acidic shift in the i.e.p., an indication of anion specific adsorption (the effect increasing in the order listed). Silicon nitride did not exhibit a measurable i.e.p. in the presence of $(\text{NaPO}_3)_6$. This behaviour was due to strong surface adsorption which occurred as the result of high negative charge density associated with this multivalent acid. Of the remaining oxo anions in Fig. 14, their affect on the electrokinetic behaviour of Si_3N_4 is

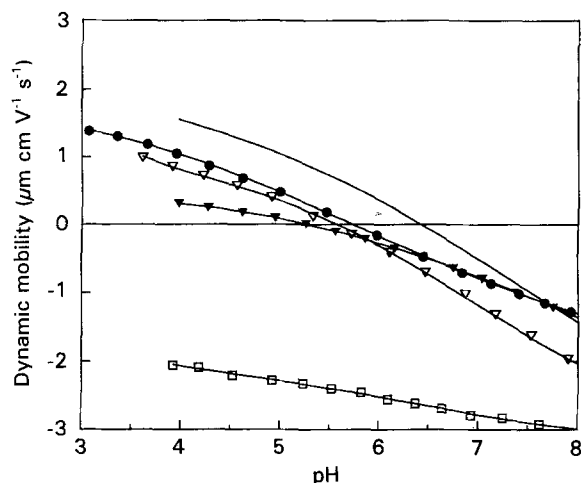


Figure 14 Electrokinetic titration curves for Si_3N_4 in the presence of various oxyanions compared to $0.01 \text{ mol l}^{-1} \text{ NaNO}_3$ solution (—): $0.005 \text{ mol l}^{-1} \text{ K}_2\text{HPO}_4$ (●), Na_2SiO_3 (▽), K_2SO_4 (▼); $0.0017 \text{ mol l}^{-1} (\text{NaPO}_3)_6$ (□).

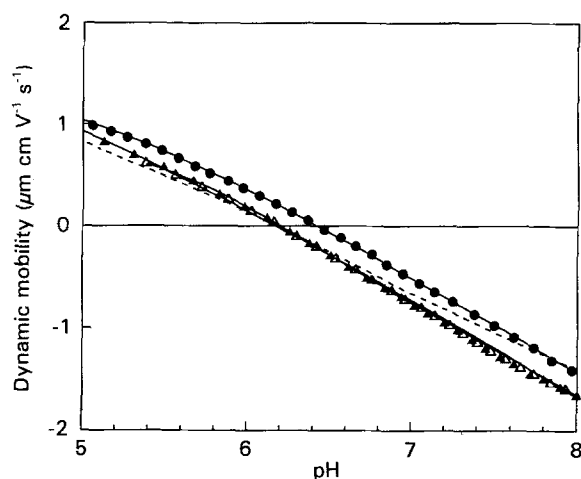


Figure 16 Electrokinetic titration curves for Si_3N_4 showing the effects of carbonate specific adsorption. ●, $0.01 \text{ mol l}^{-1} \text{ NaNO}_3$; ▲, $0.005 \text{ mol l}^{-1} \text{ Na}_2\text{CO}_3$; △, $0.01 \text{ mol l}^{-1} \text{ Na}_2\text{CO}_3$; ---, CO_2 contaminated $0.01 \text{ mol l}^{-1} \text{ NaNO}_3$.

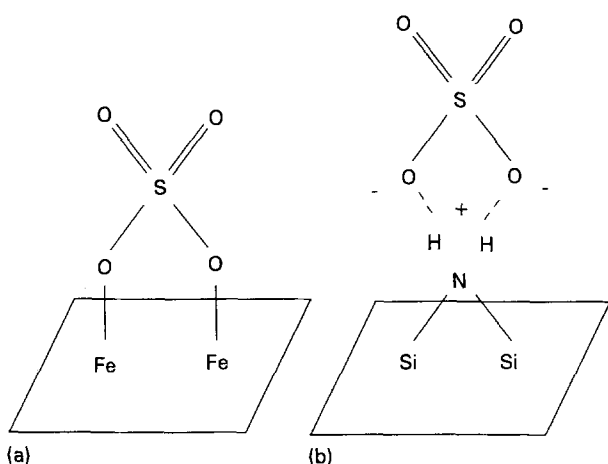


Figure 15 Surface complexation mechanisms for sulphate oxyanion ligand on (a) iron oxide (bidentate bridging complex) and (b) silicon nitride (weak ionic complex with silazane group).

related to their relative acid–base properties and ligand affinity for the Si-OH and $\text{Si}_2=\text{NH}$ surface groups.

The apparent surface affinity of sulphate and phosphate for Si_3N_4 is reversed from the order generally found for iron oxides [31–33]. On the amphoteric (single-site) iron oxide surface, oxo anions form a strong inner-sphere complex by ligand exchange with two adjacent surface hydroxyls (bidentate bridging complex) as shown in Fig. 15a. The tendency to form surface complexes appear to be largely dependent on the stability of the solution phase metal–anion complex [34]. The reverse order on Si_3N_4 could indicate that $\text{Si}_2 = \text{NH}$ surface sites plays the dominant role in uptake of dissolved oxo anions by this system. On the zwitterionic (two-site) Si_3N_4 surface, the relatively acidic silanol OH^- is less labile and, as a result, the adsorption most likely occurs at the positive $\text{Si}_2 = \text{NH}_2^+$ sites. A proposed adsorption mechanism for oxo anion adsorption on Si_3N_4 is shown in Fig. 15b.

This complex is probably weaker and more ionic in nature than the inner-sphere complex formed with transition metals, and may be largely stabilized by hydrogen bonding between the silazane (or adjacent silanol) proton and the acidic oxygen of the adsorbed anion. A bidentate complex between adjacent $\text{Si}_2 = \text{NH}_2^+$ sites is possible, but not probable, given the disordered and mixed-site nature of the Si_3N_4 surface. Sulphate is in the divalent SO_4^{2-} form between pH 2 and 6.4, and should form a more stable ionic complex with the positively charged surface sites of Si_3N_4 , relative to monovalent H_2PO_4^- and undissociated $\text{SiO}(\text{OH})_2$. Silicates are essentially uncharged below pH 9, however the chemical similarity between meta-silicate and the silicate-rich surface layer on Si_3N_4 may account for the relatively high affinity and larger than expected i.e.p. shift.

When carbon dioxide dissolves in water it reacts to form carbonic acid and its dissociated carbonate species. The ubiquitous nature of CO_2 and its increasing solubility in alkaline solution makes it a persistent problem in potentiometric titrations. Observed variations in the measured i.e.p. of Si_3N_4 suspensions, determined over extended periods of time, implied chemical changes were occurring on the surface which could not be accounted for adequately. This anomalous behaviour was at first attributed to powder ageing effects, however, closer scrutiny of the data suggested specific adsorption of carbonate. It is known that CO_2 strongly adsorbs on iron oxide [35, 36], where ligand exchange and hydrogen bonding occurs between carbonate and surface hydroxyl groups. In order to test the carbonate adsorption hypothesis for Si_3N_4 , titrations were performed in Na_2CO_3 solutions. This data is presented in Fig. 16; it confirms the chemical adsorption of carbonate on the Si_3N_4 surface. The i.e.p. is shifted to the acidic side a maximum of only 0.2 pH units (from 6.4 to 6.2), however this shift is reproducible and coincidentally equivalent to the observed variations in i.e.p. The effect may seem small, but shifts of this magnitude are significant enough to

interfere with the interpretation of surface chemical studies based on electrokinetic and potentiometric data. Carbonate adsorption might also contribute to the apparent variation between results obtained at different laboratories for the same powder. It was subsequently determined that the source of CO₂ contamination was the alkaline solutions used as titrants. Consequently, base titrants should be low-carbonate and stored in such a manner as to prevent CO₂ contamination over long periods.

4. Summary

In this paper the effects of dissolved ions on the electrokinetic properties of aqueous Si₃N₄ suspensions, using an electroacoustic technique, have been examined. The results of this study are useful in understanding the effects of impurities, contaminants and additives on the colloidal processing and suspension behaviour of Si₃N₄ powders. For the purpose of this paper, ions are segregated according to chemical similarity and surface affinity in the following manner; 1. simple univalent electrolytes showing primarily non-specific behaviour; 2. divalent alkaline-earth metal cations which exhibit some specificity; 3. hydrolysable metal cations which are characterized by complex pH-dependent behaviour; and 4. inorganic oxo anions which adsorb strongly on oxide surfaces. The i.e.p. of a suspension, the pH of zero electrokinetic potential, becomes more acidic or basic in the presence of specifically adsorbed anions and cations, respectively. Movement of the i.e.p. was the primary basis for understanding specific adsorption effects in the present study. It was found that F⁻ adsorbed specifically, and that NH₄⁺ did not. Both of these ions are commonly found on Si₃N₄ powders. Alkaline-earth metals are common impurities in commercial powders, and are also used in oxide sintering aids. The metal ions in this group adsorbed specifically at surface Si-OH sites, with a similar affinity below pH 7.5. In contrast, the hydrolysable metal ions of the transition series exhibited widely varying behaviour and a complex pH dependence which was related to their charge density and tendency to hydrolyse. Ions in this category were used for *in situ* heterogeneous precipitation of metal oxide sintering aids directly onto the Si₃N₄ surface. The oxo anions adsorbed strongly on Si₃N₄, with their affinity depending largely on charge density and tendency to complex surface Si₂=NH groups. Within this group, carbonate adsorption represented the most significant reaction. Anomalous i.e.p. variations have been explained by the specific adsorption of carbonate in CO₂ contaminated titrants.

Overall, Si₃N₄ appeared to behave similarly to SiO₂ when interacting with cationic species. In contrast, anions appeared to interact primarily with silazane sites and as a consequence the surface affinity deviated from that found on oxide surfaces. A possible exception may have involved the adsorption of fluoride, forming a stable complex with silicon. In general, the presence of metallic impurities on or near the Si₃N₄ powder surface can be expected to decrease

surface acidity. The presence of oxygen, halides and oxo acids will cause an increase in surface acidity and a decrease in the isoelectric point.

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