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Stability of colloidal silicon nitride suspension with poly-electrolyte

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Abstract

This investigation aimed at elucidating the polymer conformation of NH_4^+ salt of poly(acrylic acid) (PAA–NH_4) and relating it to the stability of colloidal silicon nitride suspension as a function of pH values. Conformation of PAA–NH_4 on silicon nitride particle was monitored along with electrokinetic and stability responses at different PAA–NH_4 concentration. The conformation of PAA–NH_4 has been identified by the use of titration experiments, from which the values of α and their corresponding pH can be roughly characterized by four stability regions. The stability properties indicate that conformation of the PAA–NH_4 chain along with the electrostatic interactions is shown to be a major controlling factor in determining the stability of the slurries considered here. At the acidic pH range, polymer adsorption in the coiled form is demonstrated to have a positive contribution to the dispersion. Nevertheless, the residual polymer in the stretched form is detrimental to the stability properties in the alkaline pH range. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Suspension; D. Si_3N_4; Colloid; Stability

1. Introduction

The homogenization, dispersion, and stability of particles in suspensions are important in the processing of high-performance ceramics produced by conventional slurry consolidation methods such as tape casing and slip casting. In industry, it is generally accepted that the driving force and efficiency of sintering is influenced by the basic powder properties such as purity, grain size, and chemical heterogeneity. However, recent studies suggest that the packing and distribution of particles throughout the green body control the porosity and microstructure and play an important role in determining the reliability of the final product [1–4].

Polyacrylic acids are frequently used to disperse oxide particles such as alumina [5,6], rutile, and hematite [7,8]. The adsorption of polyacrylic acids on these particles was found to be responsible for the dispersion. It was shown that polyacrylic acid strongly adsorbed on positively charged particle surfaces from an acidic pH to pH_{IEP} (defined as the pH where the charge at the stern layer is zero). Above pH_{IEP}, the particles become negatively charged and start to repel the polymer. Recently, investigation of the polymer conformation in the adsorbed state has been made by the use of fluorescence spectroscopy, under fixed pH conditions, the stretched polymer (which dangles into the liquid at the solid/liquid interface) gives better flocculation than the coiled polymer (which sits at the interface) [9–13]. However, whether the above reported results are applicable to the system of silicon nitride remains to be determined.

On the other hand, the effectiveness of acrylate-based polymers, such as polyacrylic acid and ammonium polymethacrylate, as dispersants for silicon nitride was demonstrated in the past [14–21]. These studies emphasized the general rules of dispersion and well-dispersed silicon nitride suspension can only be obtained in both the neutral and alkaline pH range by the application of polyelectrolyte. In the acid pH range, the powder underwent agglomeration (with a large median agglomeration size) even in the presence of the polyacrylate. However these studies have focused on relatively dilute suspension and narrow ranges of polymer concentration. The full scope of stability associated specifically with the conformation of an acrylate-based polymer has not been examined.

This paper describes the results of an experimental investigation that has been focused on the Si_3N_4–H_2O–PAA–NH_4 system. The ionization chemistry and conformation changes of ammonia salt of poly(acrylic acid)

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($PAA–NH_4$) were characterized by the potentiometric titration method. Interaction of $PMAA–NH_4$ with the Si_3N_4 surface was analyzed using electrokinetic measurements. The settling experiments and rheological characterization were used to determine the degree of stability. The effects of polymer concentration and pH were evaluated.

2. Experimental procedure

2.1. Powder and dispersant characterization

Commercially available α-Si_3N_4 particulates (LC-12N, H. C. Starck) and $PAA–NH_4$ (D305, Chukyo Yushi Co., Nagoya, Japan) were used as raw materials in this investigation. The physical properties of Si_3N_4 particulate are shown in Table 1.

The polyelectrolyte used was NH_4^+ salt of poly(-acrylic acid). The $PAA–NH_4$ structure and dissociation reaction shown below illustrate the functional groups of carboxylic acid that can be COOH or dissociated to COO^-. The pH value was adjusted with standardized analytical-grade HCl and NaOH solutions (0.1 to 1.0 N). Analytical-grade NaCl was used to adjust the ionic strength to the desired values.

2.2. Experiment methods

2.2.1. Potentiometric titration experiments

The procedure of using potentiometric titration to determine polymer behavior has been well established and details of this method can be found in the literature [22–24].

A known amount of the $PAA–NH_4$ in the range of $0.098\sim1.47$ mg/m^2 (per unit surface area of solids) was diluted with de-ionized water to approximately 25 ml. This solution was then sealed in the titration cell and the pH was adjusted to 12 to ensure that $PAA–NH_4$ was fully dissociated. The first-derivative titrations were then conducted with 0.5 N HCl and the distance between peaks was recorded. Fraction of dissociated carboxyl groups at a specified pH can then be calculated by the ratio of the amount of titrant that reacted with the sample.

Table 1
The physical properties of Si_3N_4 particulate[a]

Properties	Specification	
BET specific area	18–21 m^2/g	
Green density	1.8–2(g/cm^3)	
Particle size distribution by laser diffraction	X_{90}	1.5 μm
	X_{50}	0.6 μm
	X_{10}	0.25 μm

[a] H. C. Starck Inc.

$$\alpha = \frac{\text{The amount of titrant reacted at a specified pH}}{\text{The amount of titrant reached at pH} = 12}$$

2.2.2. Zeta potential measurements

The experimental procedures conducted in the present study were strictly performed and these as-received powders are believed to be free of any intentionally added manufacturing aids which might alter their colloidal behavior in a manner uncharacteristic of the pure solid. For the purpose of eliminating the possible unknown history-dependent contamination introduced on the powder surface during normal shipping and handling procedures [25], the following rinse process was taken. To affirm the IEP of the Si_3N_4 colloid, the as-received powders were first rinsed with de-ionized water, and the washed powder were then dried overnight at low temperatures (approx 40°C) before colloid preparation. Electrophoretic mobility was measured and used to calculate zeta potential. The 2 vol% Si_3N_4 samples were centrifuged and the supernatant was carefully decanted into a beaker. Subsequently, a very minute amount of sediment was re-mixed with the supernatant. The samples were ultrasonicated and stirred for 15 min prior to the measurement to ensure that only the mobility of the single particle was measured. The zeta potential of Si_3N_4 with various amounts of $PAA–NH_4$ and pH was determined by Zeta III, zeta meter, USA.

2.2.3. Settling experiments

The 2 vol% Si_3N_4 suspension with various amounts of $PAA–NH_4$ was ultra-sonicated and stirred for at least 1 h. The suspension was poured into a graduated and sealed test tube to determine the variation of sediment volume at various intervals.

2.2.4. Rheological measurements

The 10 vol% Si_3N_4 suspension with various amounts of $PAA–NH_4$ and pH values were milled for 24 h. Each resultant suspension was analyzed directly by measuring viscosity to determine the degree of coagulation of particles in solution. Rheological characterization was performed on rheometers (model DV II, Brookfield Engineering Laboratories, Inc., USA) at 25°C with a concentric cylinder measurement geometry. Suspensions were subjected to a high rate of 100 s^{-1} to break up any initial network structure, then lower rates were then employed.

3. Results and discussion

3.1. Polymer conformation of *PAA–NH₄* in solvent

An important characteristic for the ionizable polymer is their ability to undergo expansion from a coiled to a stretched conformation as charge density increases along the flexible chain. This cooperative transition is due to electrostatic repulsion between neighboring ionized sites. Leyte and Mande [26] interpreted their titration curves for poly(methacrylic acid) (PMAA) in terms of a similar reversible transition between two stable conformational states and confirmed these results using spectroscopic methods [27]. In PMAA, the transition occurs over a relatively narrow range of ionization, roughly $0.1<\alpha<0.3$, as evidenced by a fairly abrupt change in the slope of the titration curves in the region. In this case, stabilization of the coiled structure at low α (low pH) is prompted by the hydrophobic interactions of the α methyl groups. Mathieson and Mclaren [28] examined PAA (Mw$=2.6\times10^6$), which lacks the hydrophobic side groups of PMAA, and found a similar, although less-pronounced, transition in the titration data that occurs at intermediate α values (roughly $0.45<\alpha<0.65$). These authors distinguished four regions in the titration curve, analogous to those identified by Wada [29], and they associated these regions with conformational changes in PAA.

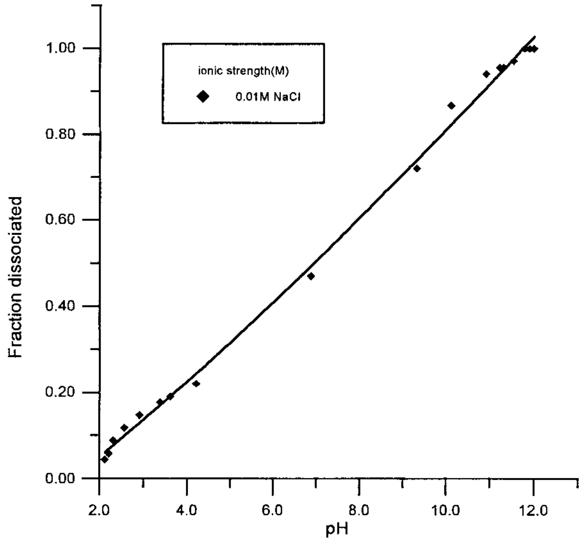

Fig. 2. Typical behavior of fraction of dissociated carboxyl group as a function of pH for PAA–NH_4 concentration of 0.49 mg/m^2.

The results of titration with and without PAA–NH_4 addition and its corresponding first-derivative plot are shown in Fig. 1. For the case of PAA–NH_4 addition, more titration amount is needed and its corresponding first-derivative peak intensity decreases with increasing PAA–NH_4 concentration. It could be attributed to the dissociation of PAA–NH_4 in the solution producing COO^- groups and NH_3 groups; as the dissociated amounts increased with PAA–NH_4 concentration, the more reacting amount of H_3O^+ with COO^- and NH_3 groups to form COOH and $NH_4{}^+$, respectively. Fig. 2 depicts the fraction of dissociated functional groups as a function of pH. As pH increases, the fraction dissociated (α) increases from ~0 to ~1 in the range of 0.098 ~1.47 mg/m^2. The curves in Fig. 3 are qualitatively similar to those found by Mathieson and Mclaren [28], for PAA dissociation, the region labeled 'A' and characterized by a sharp upward curvature is attributed to instabilities that possibly caused by precipitation of the coiled form of PAA–NH_4. Region 'B' represents ionization of the coiled state, region 'C' is the transition region that is associated with coil expansion, and 'D' represents ionization of the stretched state. The values of α and pH that roughly corresponded to these four stability regions are listed in Table 2. An interesting point is that extrapolation of pka values to $\alpha=0$ yields a value of 3.0. This value is consistent with those for simple organic acids which only have one acid group [5].

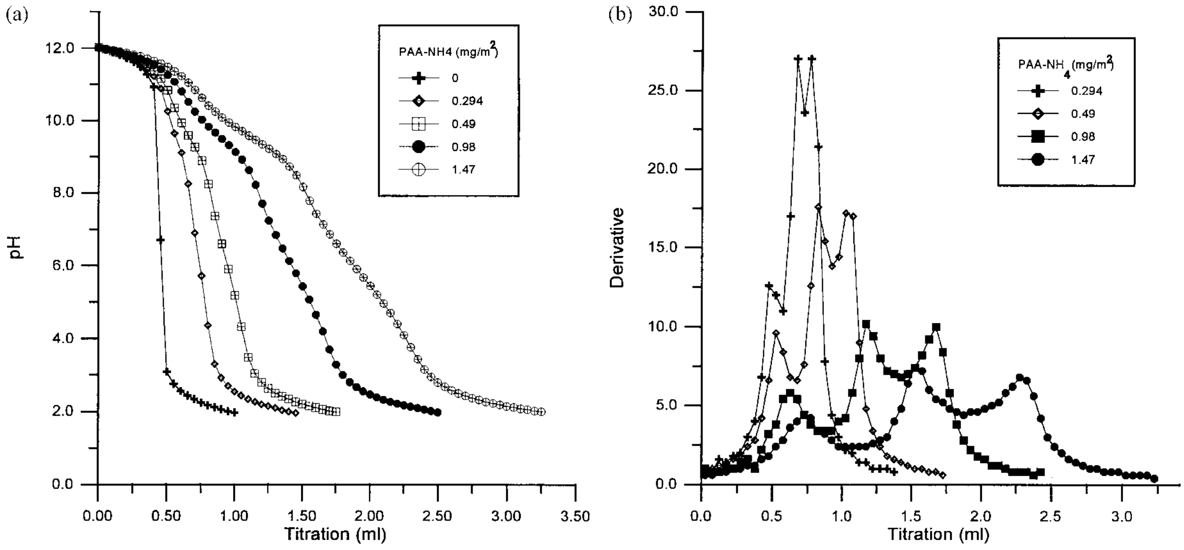

Fig. 1. (a) Effect of PAA–NH_4 concentration on the typical titration curves and (b) its corresponding first-derivative plot.

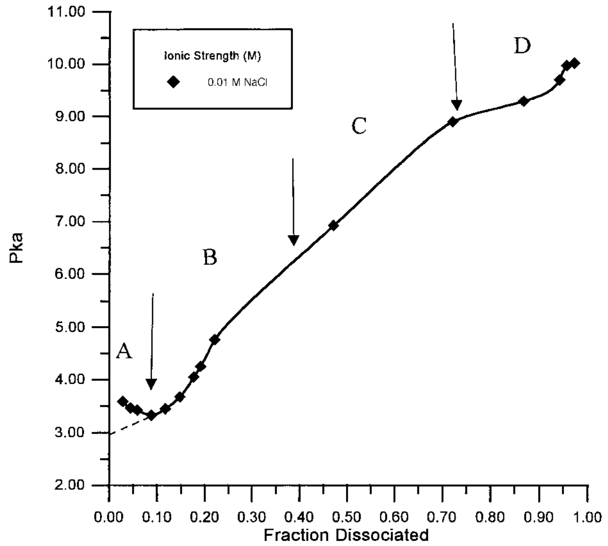

Fig. 3. Dissociation reaction constant (PKa = −logKa) of carboxyl group for PAA–NH_4 as a function of fraction dissociated.

In this condition the polyelectrolyte chains approach insolubility and are unstable for region A. As pH is increased, the number of negatively charged sites also continually increases until the polyelectrolyte is effectively ionized near pH = 12 and $\alpha \sim 1$ for region D. Where the polyelectrolyte is in the form of relatively large expanded random coil (~10 nm) in solution [22].

In similar experiments for PMAA–Na titrated using the automatic titration unit in the first-derivative titration mode. The distance between two peaks is reasoned to represent the amount of titrant required to reach the end point and depends linearly on the amount of PMAA–Na titrated [5], but the detail for the two peaks has not been well described. In the present study, the three peaks of typical first-derivative plot in Fig. 1(b) can be well defined from the viewpoint of Pka and the possible reactions are represented by Eqs. (1)–(3):

$$H_3O^+ + OH^- \longleftrightarrow 2\,H_2O \quad (1)$$

$$H_3O^+ + PAA^- \longleftrightarrow PAA - H + H_2O \quad (2)$$

$$H_3O^+ + NH_3 \longleftrightarrow NH_4^+ + H_2O \quad (3)$$

Table 2
Approximate conformational stability regions for PAA–NH_4, based on analysis of potentiometric titration data

Region	α Range	pH range	State
A	$\alpha < 0.09$	< 2.3	Unstable
B	0.09–0.4	2.3–6.9	Coiled (a state)
C	0.4–0.7	6.9–9.3	Transition
D	>0.7	>9.3	Stretched (b state)

In the range of pH (= ~10 to ~12) for peak1, as pka (OH^-) > pka (PAA^-) > pka (NH_3), free hydronium ions react with OH^- ions preferentially. Therefore with increasing PAA–NH_4 concentration, the amount of titrant reacted does not change and hydrous reaction dominates in this range. In the range of pH (= ~7 to ~10) for peak2, even pka(OH^-) > pka (NH_3) > pka (PAA^-), the reacted amounts decrease with the decreasing amount of OH^- ions and Eq. (3) dominates in this range. Consequently titration amount increases with increasing PAA–NH_4 concentration. In the range of pH = ~4 to ~7 for peak3, the reacted amounts decrease with the decreasing amount of NH_3, Eq. (2) dominates in this range. While in the range of pH = ~2 to ~4, as fraction dissociated (α) decreases to ~0 and pka decreases to ~3.0, titration amount does not change with increasing PAA–NH_4 concentration. These results can be identified in Fig. 4, the distance between peak1 and peak3 increases with PAA–NH_4 concentration, and a linear curve was established with $R^2 > 0.99$ for a known PAA–NH_4 concentration.

3.2. Interaction of PAA–NH_4 with the Si_3N_4

Fig. 5 shows the dependence of Si_3N_4 suspension zeta potential on pH values without PAA–NH_4 addition. The zeta potential changes from −46 mv at pH = 11 to +45 mv at pH = 3, with an isoelectric point (IEP) at about pH = 6.3. Above pH = 6.3, it exhibits a negative zeta potential that gradually increases with pH value. The isoelectric point of silicon nitride has been shown to vary with the ratio of $-Si_2{=}NH$ to –Si–OH surface groups, which is powder specific [25] due to different manufacturing procedures and the value is in agreement

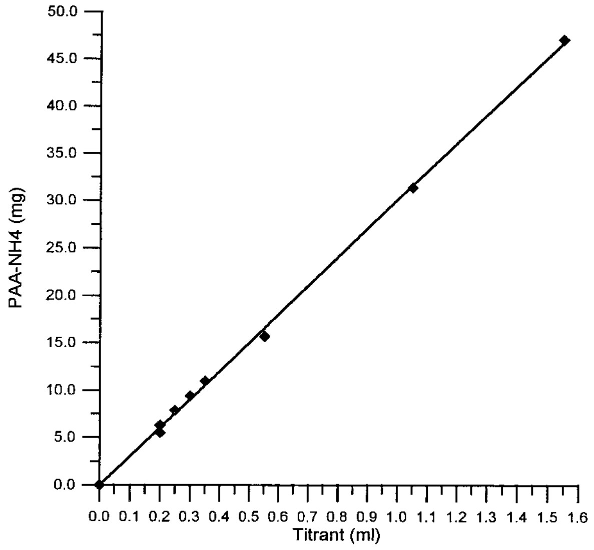

Fig. 4. Linear relationship between the amount of PAA–NH_4 titrated and the mole equivalent of titrant corresponding to the distance between peak1 and peak3.

with the reported electroacoustic behavior of silicon nitride powder [15,16]. The electrokinetic of Si_3N_4 in the presence of PAA–NH_4 as Fig. 6 shows that for the pH range used PAA–NH_4 dosage results in a more negative zeta potential than the one without addition. As is expected, at these pHs the polyelectrolyte is negatively charged and hence imparts a higher charge density on the particles. The value zeta potential gradually increases (i.e. became more negative) with addition until a plateau region is reached. Nevertheless, the charge properties of the PAA–NH_4-modified powder surface are basically determined by the equilibrium pH, the dosage of PAA–NH_4 decrease the zeta potential significantly for pH = 3~5 while for pH = 9~11 nearly no decrease can be seen. In the acid pH range, where α approaches zero and the free polymer is essentially neutral. It is evident as reflected by Table 2 that the polymer is in the coiled form. More likely, the presence of coiled-polymer chains can disturb the hydrodynamic plane of shear, shifting it further out from the particle surface. Because potential decreases exponentially with

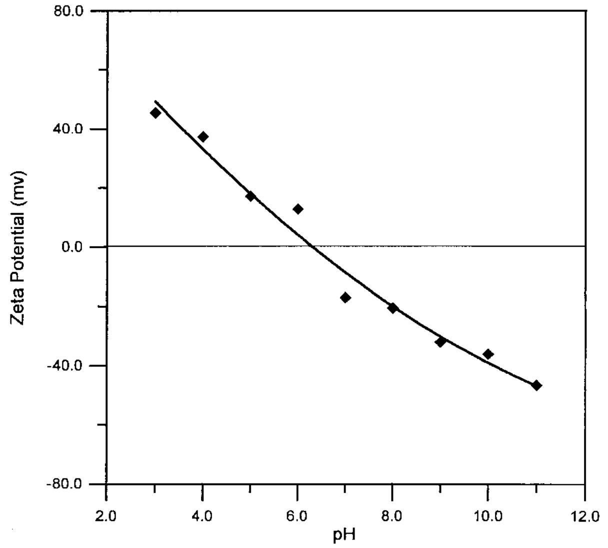

Fig. 5. Effect of pH on the zeta potential for Si_3N_4 suspension in the pH range from 3 to 11.

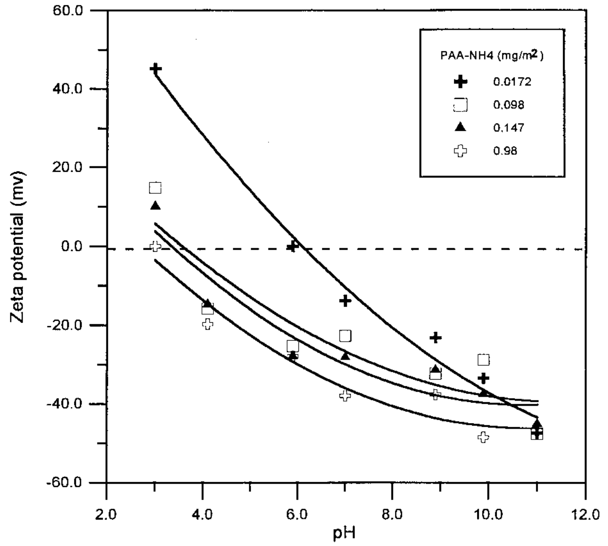

Fig. 6. Effect of pH and PAA–NH_4 concentration on the interfacial charge behavior of silicon nitride in aqueous media.

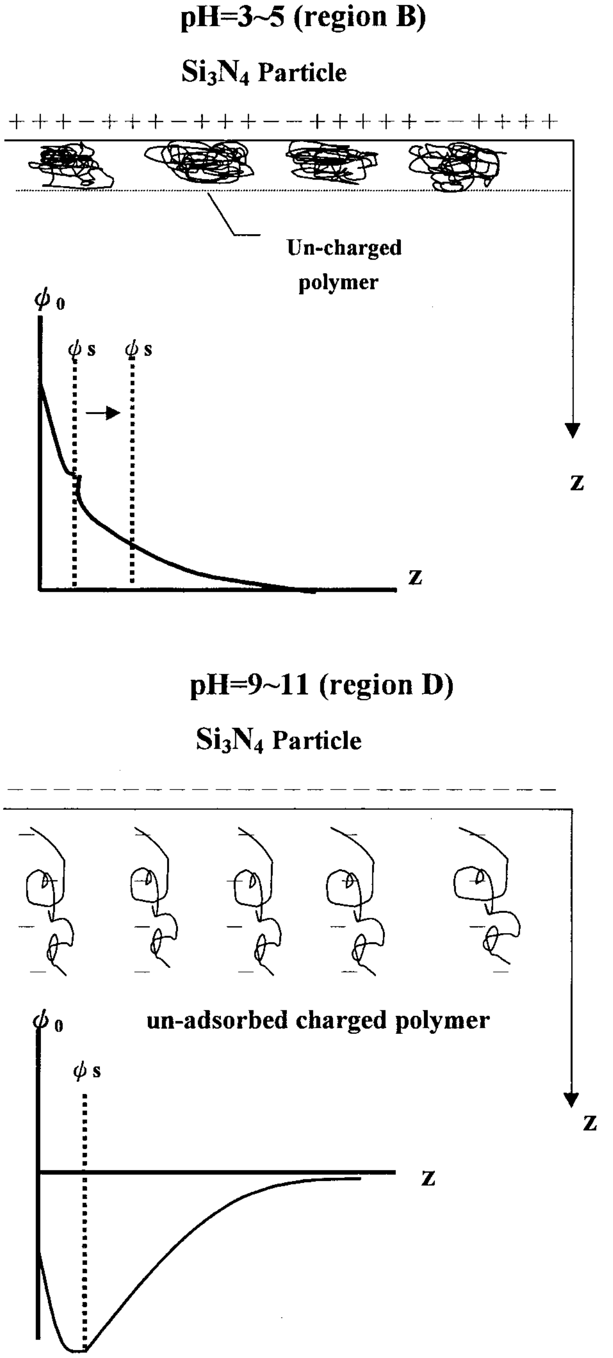

Fig. 7. Schematic illustration depicting PAA–NH_4 interactions at the solid–solution interface, as a function of pH. Possible surface conformations are shown, with associated potential-distance diagrams, indicating surface potential (ϕ_0) and shear-plane potential (ϕ_s).

distance [23], the modified shear plane will experience a lower potential. The other interaction type, which is found at strongly alkaline pH values where α approaches a value of 1 as shown for pH = 9~11 in Fig. 6. The weak interaction between PAA–NH4 and particle as revealed by this electro-kinetic curve is attributed to the mutual repulsion between the highly ionize-stretched polymer and negative charged particle surface. The phenomenon is shown schematically in Fig. 7.

3.3. *Stability of colloidal suspension*

The stability properties indicate that the dispersion of colloidal silicon nitride particles depends on pH values, the conformational characteristics of PAA–NH4, and silicon nitride surface chemistry.

Fig. 8 shows that the stability of silicon nitride particles without PAA–NH4 dosage is controlled by electrostatic interactions as indicated by maximum sediment volume and viscosity at the iso-electric point. No repulsive force exists in the pH range near the isoelectric point, and the large attractive van der Waals force produces an attractive, touching particle network. This is in agreement with the reported dispersion behavior of the silicon nitride powder, [15] a critical of 40 mv zeta potential was required for the dispersion of this powder in suspensions. The stability of silicon nitride particles in the presence of PAA–NH4 is strongly dependent on pH. As shown in Fig. 9 the three pH values chosen for further discussion can well represent the corresponding three characteristic type of stability properties of silicon nitride suspension. To investigate the mechanism of

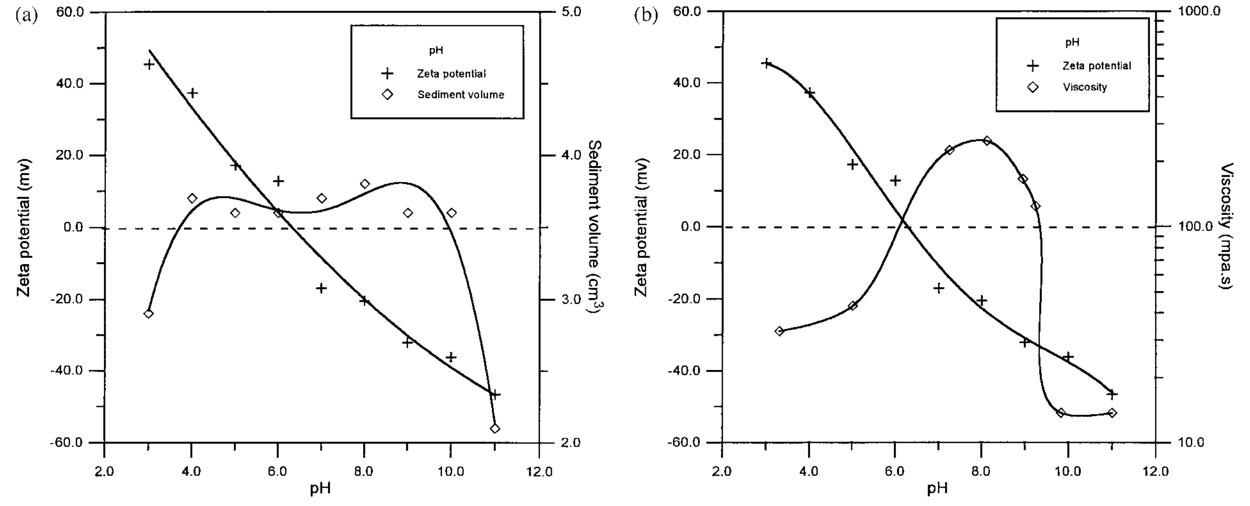

Fig. 8. (a) Effect of pH on tha zeta potential and sediment volume for Si_3N_4 suspension in the pH range from 3 to 11. (b) Effect of pH on the zeta potential and viscosity at a shear rate of 100 S^{-1} for Si_3N_4 suspension in the pH range from 3 to 11.

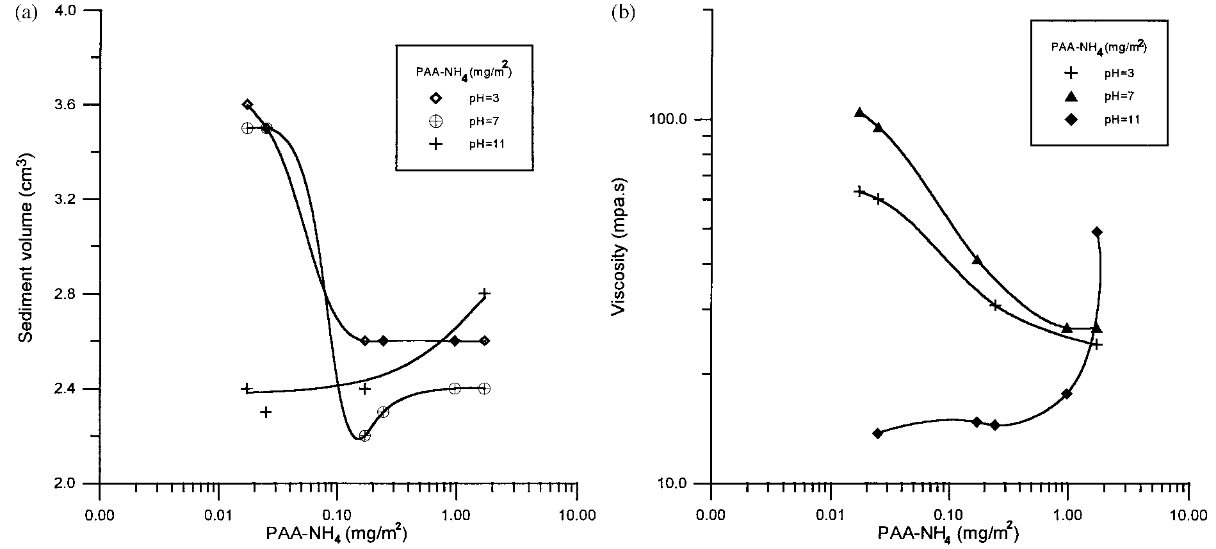

Fig. 9. (a) Effect of PAA–NH4 concentration on the sediment volume for Si_3N_4 suspension at pH = 3, 7 and 11, respectively after 53 h of sedimentation. (b) Effect of PAA–NH4 concentration on the viscosity under a steady rate (100 s^{-1}) for aqueous Si_3N_4 suspension (10 vol%) at pH = 3, 7 and 11, respectively.

stability of silicon nitride using PAA–NH$_4$ at various pHs, the values of electroacoustics and stability properties as a function of the PAA–NH$_4$ dosage are compared in Figs. 10–12. For pH = 3, the minimum sediment volume and viscosity occur at the completion of monolayer coverage of the polyelectrolyte on the particles, which corresponds to no charged polyelectrolyte-coated particles. This indicates that no electric repulsive forces exist in the presence of PAA–NH$_4$ and polymer adsorption in the coiled form is demonstrated to have a positive contribution to the stability in this acidic pH range. The stability properties as a function of the PAA–NH$_4$ dosage at pH = 7 is shown in Fig. 11. The sediment volume and viscosity decrease with increasing zeta potential. It reflects that the degree of flocculation decreases with an increase in the zeta potential and the dispersion properties of silicon nitride suspension with the PAA–NH$_4$ dosage are basically dominated by the surface (interfacial) charge properties of the powder in neutral pH values. On the other hand, as Fig. 12 shows that the suspension is a stable colloid at a critical dosage of PAA–NH$_4$; with further dosage, it reflects a transition from stabilization to flocculation. As shown for pH = 11, the weak interaction between polymer and particle as revealed in electroacoustics suggests that no decrease in zeta potential and non-adsorbed highly stretched polyelectrolyte is consequently appreciably present in solution when PAA–NH$_4$ is added. It indicates that residual polymer in the stretched form is detrimental to the stability properties and the dispersion properties in the presence of PAA–NH$_4$ is basically dominated by the surface (interfacial) charge primarily between the silicon nitride particles in the alkaline pH range.

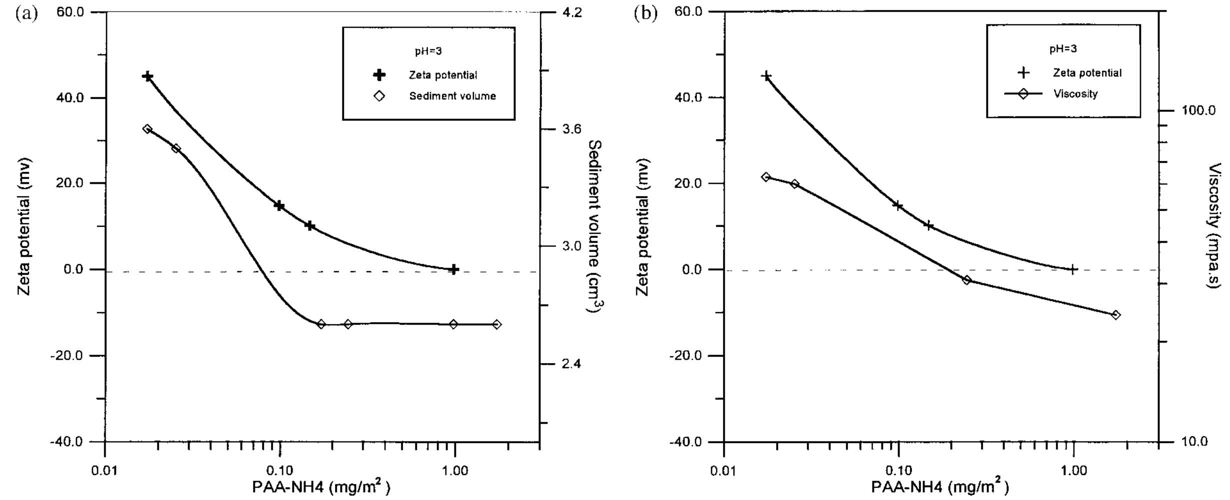

Fig. 10. (a) Effect of PAA–NH$_4$ concentration on the zeta potential and sediment volume for Si_3N_4 suspension at pH = 3. (b) Effect of PAA–NH$_4$ concentration on the zeta potential and viscosity at a shear rate of 100 S^{-1} for Si_3N_4 suspension at pH = 3.

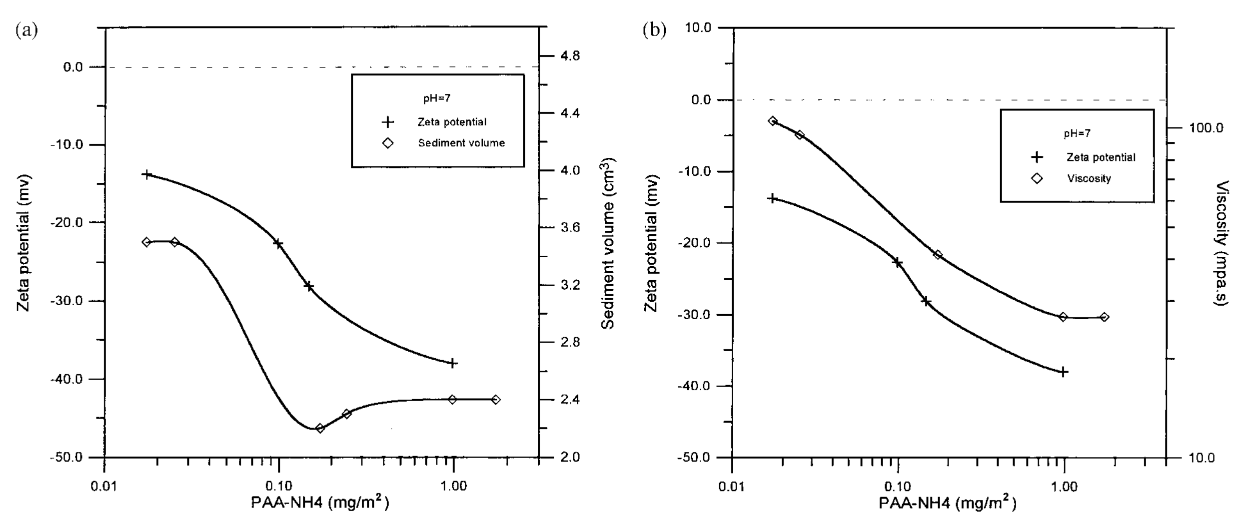

Fig. 11. (a) Effect of PAA–NH$_4$ concentration on the zeta potential and sediment volume for Si_3N_4 suspension at pH = 7. (b) Effect of PAA–NH$_4$ concentration on the zeta potential and viscosity at a shear rate of 100 S^{-1} for Si_3N_4 suspension at pH = 7.

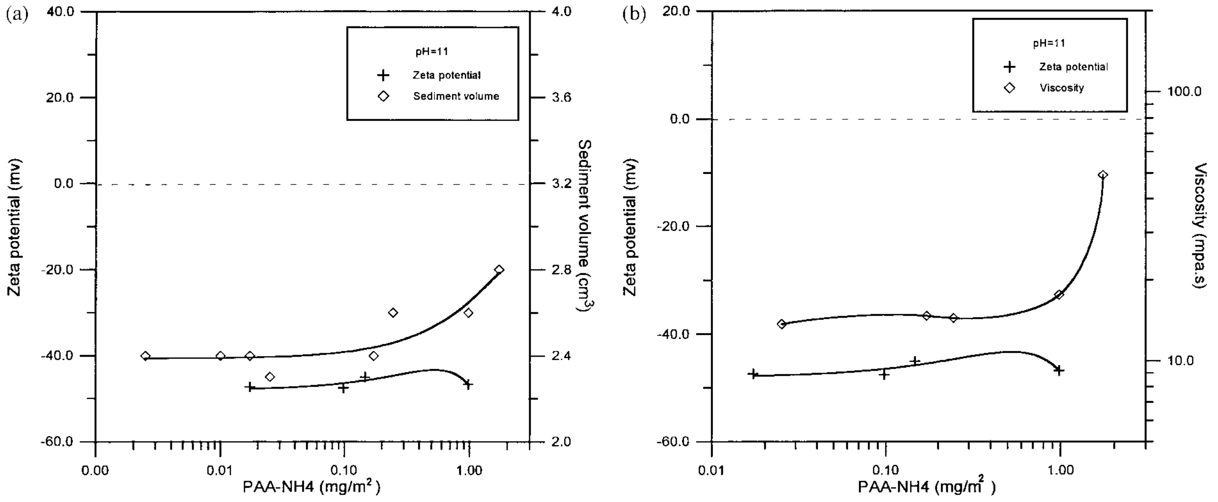

Fig. 12. (a) Effect of PAA–NH_4 concentration on the zeta potential and sediment volume for Si_3N_4 suspension at pH = 11. (b) Effect of PAA–NH_4 concentration on the zeta potential and viscosity at a shear rate of 100 S^{-1} for Si_3N_4 suspension at pH = 11.

4. Conclusion

Based on the above experimental results and discussion, the following conclusion can be drawn.

1. Titration data indicates that as the pH is increased, the number of negatively charged also continuously increases until the polyelectrolyte is effectively ionized near pH = 12, where $\alpha \sim 1$. In the meanwhile, the extrapolation of Pka value to $\alpha = 0$ yields 3. The three peaks of typical first-derivative plot of PAA–NH_4 can be well defined from the viewpoint of Pka and the possible reaction presented.
2. The conformation of PAA–NH_4 has been identified by the use of titration experiments, from which the values of α and pH can be roughly characterized by four stability regions. The region labelled ‘A’ and characterized by a sharp upward curvature is attributed to instabilities that possibly caused by precipitation of the coiled form of PAA–NH_4. Region ‘B’ represents ionization of the coiled state, region ‘C’ is the transition region that is associated with coil expansion, and region ‘D’ represents ionization of the stretched state.
3. Conformation of the PAA–NH_4 chain along with the electrostatic interactions is shown to be a major controlling factor in determining the stability of the slurries considered here. At the acid pH range, polymer adsorption in the coiled form is demonstrated to have a positive contribution to the stability. Nevertheless, at the alkaline pH range, the suspension is a stable colloid at a critical dosage of PAA–NH_4; with further dosage, it exhibits a transition from stabilization to flocculation. The residual polymer in the stretched form is detrimental to the stability properties.

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