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Influence of the Initial pH on the Adsorption Behaviour of Dispersant on Nano Zirconia Powder

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Abstract

The quantitative adsorption behaviour of ammonium salt of poly(acrylic acid) onto zirconia powder in aqueous solution is characterized by using UV adsorption spectrum. Adsorption isotherms of dispersant on the zirconia surface, electrophoretic mobility of zirconia particles as a function of the dispersant concentration have been investigated. The adsorption behaviour of PAA-NH_4 is dependent on the pH of the suspension and the concentration of the ammonium salt of poly(acrylic acid). The maximum amount of PAA-NH_4 adsorbed on the zirconia surface, 6·3 mg m^{-2} at pH 2·62, decreases to 2·1 mg m^{-2} at pH 12·20. The adsorption of PAA-NH_4 causes a highly negatively charged powder surface and almost same final pH value. © 1999 Elsevier Science Limited. All rights reserved

Keywords: adsorption, dispersant, suspensions, surfaces, ZrO_2.

1 Introduction

The quality of ceramics produced by wet forming process is determined mainly by the state of the suspension.[1,2] The good dispersion of particles gives optimum packing state which influences the sinterability in the firing process and thus the physical and chemical properties of the final product.[3] The suspension properties are determined by attractive and repulsive forces. Attractive van der Waals forces can be countered by repulsive forces resulting from either overlapping of the electrical double layers and layering of materials adsorbed on the surface. Polymers and polyelectrolytes have long been widely used in ceramic slurry processing for their distinctive advantages over inorganic agents, especially for high-tech ceramics.[4–6] They combine electrostatic and steric mechanisms to electrosteric mechanisms. By adsorption on the particle surface, these additives cause a change of the surface charge resulting in a change of the double layer repulsion. To disperse ceramic powders in aqueous suspensions with polyelectrolyte addition, several critical factors such as the pH,[7] the surface chemistry of powders,[8] the degree of polyelectrolyte[9] and the quality of polyelectrolyte[10] must be understood and controlled. Numerous studies[11–13] have been published concerning the stability of suspension systems containing polymer or polyelectrolyte. According to the work of Cesarano and Aksay[14,15] the required polyelectrolyte concentration decreased as the pH increased. However, at high solid loadings, the presence of excess dissociated polyelectrolyte species which produced high ionic strength degraded the stability of such suspensions. There exist an optimum amount of dispersant and an optimum pH range in producing concentrated slurries.[16] For slurries having high solid contents, two parts made up the income of ionic strength. One is the dissociated polyelectrolyte, another comes from the acid or basic needed to adjust the pH of the slurries. However, little attention has been paid to the later factor, the effects of the initial pH on the properties of suspensions.

The intent of this paper is to give a clear understanding of the quantitative adsorption of ammonium salt of poly(acrylic acid) onto zirconia powder by using UV adsorption spectrum. The adsorption behaviour of polyelectrolytes at different pH range is investigated. The initial pH influence on the adsorption is examined to characterize

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the zeta potential, conductance and the relation to the adsorption of PAA-NH_4.

2 Experimental Procedure

2.1 Starting materials

The powder used was commercially available 3Y-TZP (supplied by Shenzhen Nanbo Company of China). The specific surface area of the powder was around $15\,m^2\,g^{-1}$ as measured by nitrogen adsorption. The average particle size observed by TEM is 25 nm. Technical index of the powder is listed in Table 1. A polycletrolyte dispersant used in the preparation of dispersed zirconia slurries was the ammonium salt of poly(acrylic acid) (abbreviated as PAA-NH_4) with molecular weight as 5000. Deionized water was used in dissolving dispersant and making slurries. The pH of zirconia slurries was adjusted via diluted analytical grade HCl and NaOH. Analytical grade NaCl was used to adjust the ionic strength of diluted zirconia suspensions which were subjected to the measurement of zeta potential.

2.2 Slurry preparation

Solution pH which was adjusted by adding analytical grade HCl and NaOH is measured as initial pH values. The dispersant was then dissolved in the treated water. A specific amount zirconia powder was then gradually added to the solution. The suspension was deagglomerated by using a high-energy ultrasonic horn and then transferred into a polyethylene bottle which was loaded with zirconia grinding media. The slurry was agitated by a turbomixer (Turbula, Maschinenfabrik, Basel, Switzerland) for 1 to 20 h.

2.3 Property measurement

2.3.1 Adsorption of PAA-NH_4

Aqueous suspension of 10 wt% Y-TZP with different concentrations of PAA-NH_4 were prepared at pH value ranging from acidic to basic. After mixing, the suspensions were centrifuged at a speed of 10 000 rpm for 50 min to obtain clear supernatants. The residual PAA-NH_4 concentration in the supernatant was analysed by using UV spectrophotometer (UV-1602PC, Japan). Polyelectrolyte concentration measurements were determined from the adsorbance at 260 nm by using quartz spacers on a double beam spectrophotometer. The adsorbance versus concentration plots followed an identical Beer's law curve when any stock solution used was diluted with distilled water. An accuracy better than 5% was obtained. Adsorption measurements were made at room temperature at four different pH values: pH 2·62, 7·0, 11·25, 12·20, and solid/liquid ratios of 10 wt%. The concentration of PAA-NH_4 adsorbed on zirconia was then calculated by detracting the left in supernatant from the total amount of PAA-NH_4.

Table 1. Technical indexes of yttria stabilized zirconia

Purity	*Wt%*
Y_2O_3	% > 5·1
SiO2	% < 0·01
Fe_2O_3	% < 0·005
TiO_2	% < 0·01
Na_2O	% < 0·005
CaO	% < 0·005
MgO	% < 0·003
Cl^-	% < 0·01

2.3.2 Zeta potential

Suspensions were prepared by mixing 10 wt% 3Y-TZP powder in deionized water at different pH values with various concentrations of PAA-NH_4. The slurries were prepared by using the previously described procedure. After mixing, a small amount of supernatant was removed by centrifugation, one drop of the suspension was added to the supernatant. Zeta potential of the remaining powders in the supernatant was measured by using a zeta meter (Model ZetaPlus, Brookhaven Instruments). An average of at least three measurements for each sample was reported.

3 Results and Discussion

3.1 Zero point of 3Y-TZP

The effect of pH on the zeta potential of 3Y-TZP powder in a variety of NaCl solutions is shown in Fig. 1. The isoelectric point of 3Y-TZP is near to 6·8. The absolute value of zeta potential measured in 100 M NaCl solution is lower than those measured in 1 and 10 mM NaCl solution. It is due to compression of the double layer in higher ionic strength.

3.2 Adsorption of PAA-NH_4 on 3Y-TZP

Figure 2 is the UV adsorption spectrum of PAA-NH_4, The transition of $n \rightarrow \sigma$ in the group of $-C=O$ can produce the adsorption energy which located in ultraviolet range has high intensity. There is a wide peak in the range of 190 and 350 nm in Fig. 2. The highest peak position is at 238·5 nm. Two factors must be considered when selecting wavelength for measurements. One is the relative high adsorbance values, which can ensure good statistics of the measurement. Another is the stability of the data, which ensure reproducible results. We measured the dilute solution of PAA-NH_4 at the

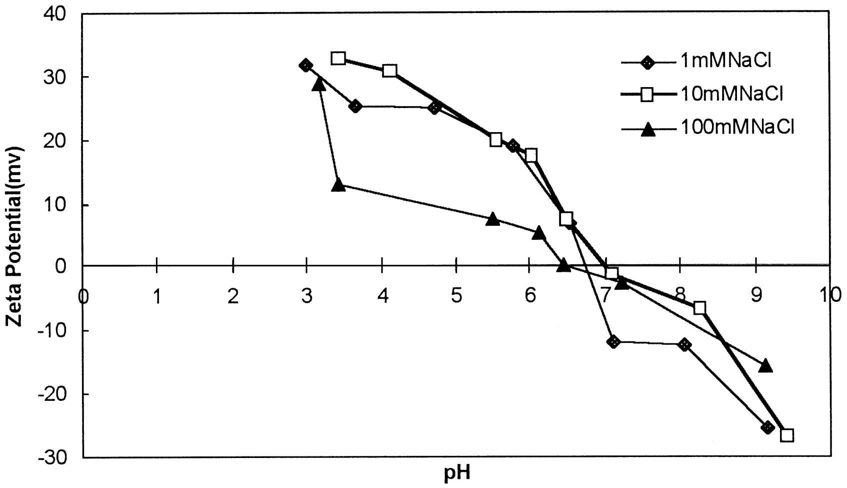

Fig. 1. Zeta potential of aqueous 3Y-TZP suspensions at different pH values.

concentration of 10 mg ml^{-1} in the range from 190 to 350 nm. 260 nm was selected as the measured wavelength. Although it did not correspond to the highest adsorbance value, but it is relatively stable compared to the adsorbance value obtained at 238·5 nm. The adsorption curves of PAA-NH$_4$ on zirconia as a function of time is shown in Fig. 3. The amount of PAA-NH$_4$ adsorbed on zirconia is dependent on the equilibration time. Note that an initial PAA-NH$_4$ concentration is 14·67 mg m^{-2}, and the initial pH is kept as constant of pH = 8·0, the adsorption of PAA-NH$_4$ on zirconia is completed in 8 h. No apparent raising is observed if the equilibrium time exceed 8 h.

The adsorption of PAA-NH$_4$ at different concentrations of PAA-NH$_4$ is measured to determine the amount of PAA-NH$_4$, required for a monolayer adsorption on the zirconia surface at different pH values. Figure 4 shows the specific adsorption of PAA-NH$_4$ on the zirconia powder at pH 2·62, 7·0, 11·25, 12·20. The amount of PAA-NH$_4$ adsorbed on zirconia is dependent on the overall PAA-NH$_4$ concentration and the pH value of the suspensions. For all pH investigated, the adsorption curves display a characteristic plateau, which corresponds to the amount of PAA-NH$_4$ required for monolayer coverage. We can see that both pH = 2·62 and pH = 11·25 has relative high adsorption. In the basic range, the adsorption amount is lower. With increasing PAA-NH$_4$ addition, the relative amount of PAA-NH$_4$ adsorbed on the surface decreased (Fig. 5). More and more PAA-NH$_4$ remains in the solution. If the solid content is low, the electrolyte will not have great influence on viscosity, otherwise, they will have deleterious effect on the suspensions, making viscosity rise vigorously. To determine the monolayer PAA-NH$_4$ adsorbance quantitatively, the data in Fig. 4 is analysed using the Langmuir monolayer adsorption equation:

$$\frac{C_e}{A_s} = \frac{C_e}{C_m} + \frac{k}{C_m}$$

The data also is plotted as C_e/A_s, versus C_e, in Fig. 6 where C_e is the equilibrium concentration of PAA–NH$_4$ in solution, A_s is the adsorbance of PAA-NH$_4$, and C_m the monolayer adsorbance of PAA-NH$_4$ k is the constant. Straight lines are observed, which indicated that these isotherms are of Langmuir monolayer-type adsorption. Because the slopes of these straight lines represent the reciprocal of the monolayer adsorption of PAA-NH$_4$, the results in Fig. 6 indicate that the amount of monolayer PAA–NH$_4$ adsorption decreases as the pH increases, and the data are 6·3 mg m^{-2} at

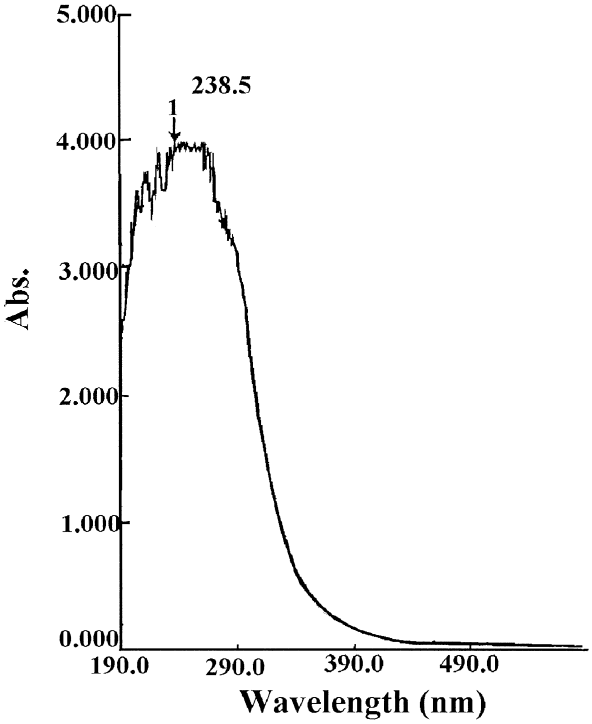

Fig. 2. The UV adsorption spectrum of PAA-NH$_4$.

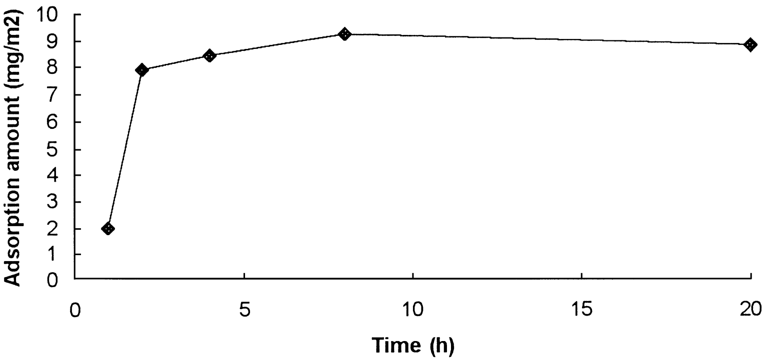

Fig. 3. Adsorption of PAA-NH_4 on 3Y-TZP surface versus equilibration time at pH 8·0.

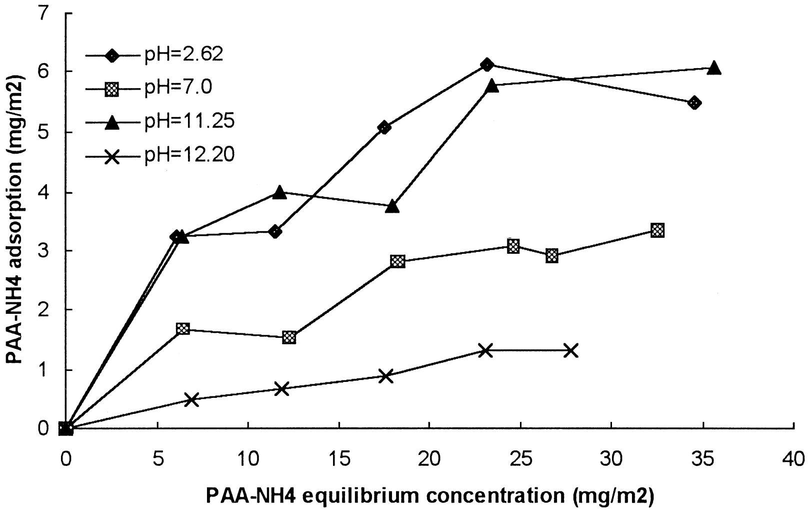

Fig. 4. Adsorption of PAA-NH_4 on 3Y-TZP surface as a function of the initial amount of PAA-NH_4 added in four different pH values.

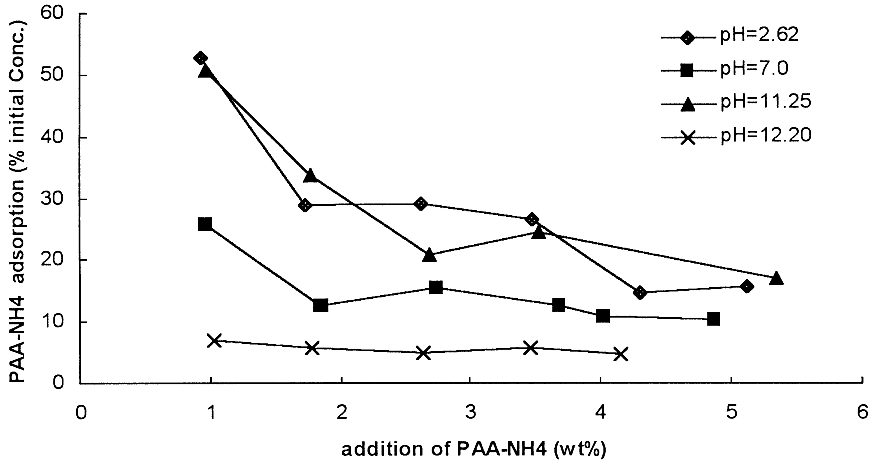

Fig. 5. Adsorption curves of PAA-NH_4 on 3Y-TZP in percent of the initial concentration as a function of PAA-NH_4 addition.

pH = 2·62, 3·8 mg m^{-2} at pH = 7·0, 5·0 mg m^{-2} at pH = 11·25, 2·1 mg m^{-2} at pH = 12·20.

An abnormal phenomenon is that similar adsorption results are obtained in initial pH 2·6 and pH 11·25. A more detailed study of the initial pH on the adsorption behaviour of PAA-NH_4 have been carried out in Fig. 7. The initial pH ranged from pH 1·02 to 13·60. The added amount of PAA-NH_4 is 3·0 mg m^{-2}. Two curves represented the two different pH values before the addition of dispersant and after the addition of dispersant. The variation of the pH, zeta potential, adsorbed amount and conductance before and after the addition of the dispersant is shown in Table 2. At initial pH = 1·02. almost complete adsorption occurred. The pH after the addition of dispersant rose to 2·06. Its zeta potential is 7·37 mv, conductance is 36984·4 μs, which correspond to 100 mM NaCl. In the strong basic range pH = 13·6, the adsorption amount decreased to 0·62 mg m^{-2},

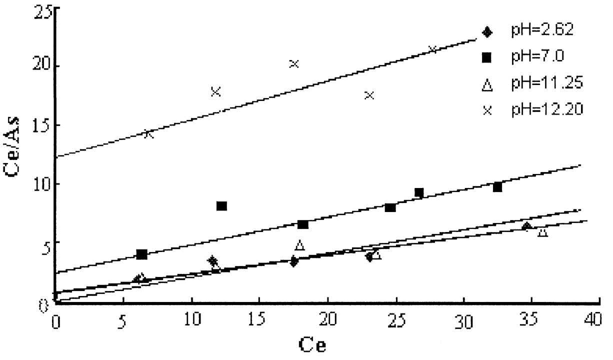

Fig. 6. Replot of Fig. 4 according to Langmuir equation.

only 20% of the total amount. Its pH value changed greatly after addition of PAA-NH$_4$, from 13·60 to 8·42. The other five points, from pH = 2·70 to 11·10, they have very similar change in pH, adsorption amount, zeta potential and conductance.

Two conclusions can be deduced from Table 2. First, the initial pH did not influence the adsorption behaviour of PAA-NH$_4$ onto zirconia powder in a wide range. In our system, from pH 2·70 to 11·10, the adsorption amount of PAA-NH$_4$ onto zirconia is almost same, around 1·0 mg m^{-2}. The main reason is due to the high buffer ability of PAA-NH$_4$. In strong acidic range, PAA-NH$_4$ can bind hydrogen ion to form weak acid HPAA and decrease the acidity of the solution.

$$\mathrm{PAA - NH_4 + HCl \leftrightarrow HPAA + NH_4Cl}$$

In the basic range

$$\mathrm{PAA - NH_4 + NaOH \leftrightarrow NaPAA + NH_3 \cdot H_2O}$$

PAA-NH$_4$ changed to NaPAA, pH of the slurries is lowered. In this study, the addition of PAA-NH$_4$ can change the slurries' pH to 8·3. Secondly, the zeta potential of the powder surface does not change much with the initial pH value except in the strong acidic range. From pH = 2·7 to 13·60, the zeta potential decreased to a constant value about −35 mv. Higher zeta potentials cannot be obtained in more basic range. It can be predicted that it will be very difficult for us to change the pH of the slurries after the addition of polyclectrolyte. Large amounts of strong acid or strong base need to be added into the solution to destroy the buffer-ability of PAA-NH$_4$. This can induce the high ionic strength and lead to compression of the double layer. The catastrophic effect of this is that the system has higher viscosity and will lose its stability.

In Ref. 15 it was reported that for the highly concentrated Al$_2$O$_3$ suspensions stabilised with PMAA, a viscosity minimum is observed at pH = 8·8. The authors attributed to two reasons. One is the fully dissociation and the maximum

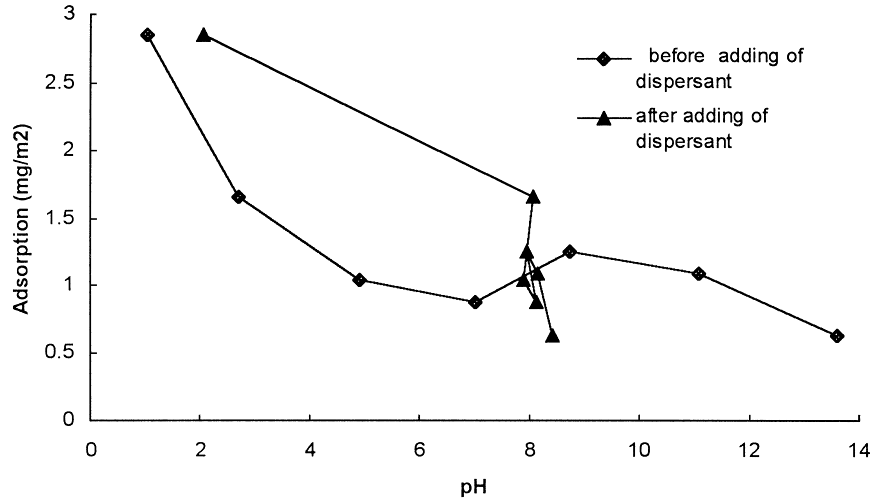

Fig. 7. The influence of pH on the adsorption of PAA-NH$_4$ on 3Y-TZP powder.

Table 2. pH, zeta potential and conductance changed in different pH value

No.	*1*	*2*	*3*	*4*	*5*	*6*	*7*
pH before adding of dispersant[a]	1·02	2·70	4·91	7·0	8·75	11·10	13·60
pH after adding of dispersant	2·06	8·06	7·90	8·05	7·9	8·15	8·42
pH of the supernant of slurry	2·28	8·19	8·34	8·14	8·30	8·30	8·56
Adsorbed amount (mg m^{-2})	2·85	1·66	1·04	0·87	1·25	1·08	0·62
Zeta potential (mv)	7·37	−33·4	−39·7	−35·7	−38·7	−36·4	−37·4
Conductance (μs)	36984·4	15924·4	14944·2	14782·9	15236·7	14658·2	14977·8

[a] Amount of dispersant added in the suspensions is 3·0 mg m^{-2}.

solubility of the polyelectrolyte, another is the high affinity type adsorption and low ionic strength. We think another main reason is due to the high buffer-ability of PMAA. Similar to our test results, no matter what initial pH it is, except in very strong acidic range, the final pH value falls to 8·3. For PMAA, its correspondent value is 8·8. The above results give us following hints, the addition of polyelectrolytes such as HPAA, PAA-NH_4, HPMAA and PMAA-NH_4 can make the slurry move to a constant pH value and have almost same zeta potential. How to lower the ionic strength in preparing concentrate suspensions is a standard in choosing the initial pH range of the slurry.

4 Conclusion

The adsorption behaviour of aqueous 3Y-TZP powder suspensions with various amounts of PAA-NH_4 at different pH values has been investigated. In four different initial pH values, the adsorption behaviour belongs to mono Langmuir adsorption. The adsorption amount correspond to the maximum value is 6·3 mg m^{-2} at pH = 2·62, 3·8 mg m^{-2} at pH = 7·0, 5·0 mg m^{-2} at pH = 11·25, 2·1 mg m^{-2} at pH = 12·20. Except in the strong acidic or basic range, i.e. pH = 1·02 and 13·6, the initial pH has little influence on the final pH, adsorption behaviour, zeta potential of the powder surface and its conductance. The main reason is due to the high buffer-ability of PAA-NH_4.

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