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Stability of Aqueous α-Al_2O_3 Suspensions with Poly(methacrylic acid) Polyelectrolyte

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Stability of aqueous α-Al_2O_3 suspensions with Na^+ salt of poly(methacrylic acid) (PMAA-Na) polyelectrolyte was studied as a function of pH. At a given pH, the transition from the flocculated to the dispersed state corresponded to the adsorption saturation limit of the powders by the PMAA. As the pH was decreased, the adsorption saturation limit increased until insolubility and charge neutralization of the PMAA was approached. The critical amount of PMAA required to achieve stability is outlined in a stability map.

I. Introduction

For many applications in ceramic processing it is desirable to sinter at relatively low temperatures and to obtain fully dense and fine-grain microstructures. One method by which these goals can be accomplished is by using submicrometer particles. In order to achieve a uniformly consolidated compact, it is also advantageous to use dispersed colloidal suspensions which contain upwards of 50 vol% solids while still maintaining relatively low viscosities of less than 1 Pa·s.

In general, suspensions can be dispersed by electrostatic, steric, or electrosteric stabilization mechanisms.[1] Electrostatic stabilization is accomplished by generating a common surface charge on the particles. Steric stabilization, on the other hand, is achieved by adsorption of polymeric additives which serve to form protective colloids. Electrosteric stabilization requires the presence of adsorbed polymer or polyelectrolyte and a significant electrical double-layer repulsion.

The main problems, related to ceramic processing, found to exist in electrostatically stabilized systems derive from aging effects and complications of processing multiphase systems.[2] The aging effects are commonly due to the solubility of particles in the suspending medium. For instance, in the case of oxide suspensions prepared with H_2O under acidic or basic conditions, the pH changes with time because of the solubility of the particles.[2] These pH changes can drastically influence rheology and suspension behavior, sometimes within a relatively short time frame of minutes to hours.[2] A second problem with electrostatically stabilizing suspensions which have more than one solid phase is that it is difficult, if not impossible, to find a pH range in which all of the particles have a substantial surface charge of the same sign so that irreversible agglomeration is prevented.[3] In general, ceramic suspensions can be stabilized electrostatically, but improvement of the suspensions to better meet the requirements necessary for ceramic processing is possible by incorporating polymeric additives.

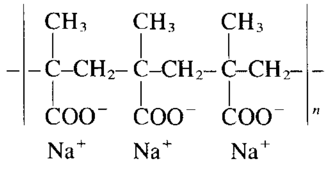
Industrial experience shows, for instance, that in highly concentrated oxide suspensions, problems related to high viscosity, aging, and processing of multiphase systems can be drastically reduced by using polyelectrolytes as dispersants or deflocculants.[3,4] However, in spite of these advantages in using polyelectrolytes to stabilize suspensions, a great deal of misunderstanding exists in the general ceramic community as to the fundamental roles of these polymeric additives. Thus, this investigation was designed to elucidate the mechanisms of polyelectrolyte stabilization and to relate them to the chemistry of the powder surface and the polymer additive. An aqueous α-Al_2O_3 system with sodium poly(methacrylic acid) (PMAA-Na) was chosen as the model.

II. Materials and Experimental Methods

(1) Materials and Chemicals

The ceramic used in this study was a very-high-purity (>99.995%), submicrometer-size, and relatively monodispersed (0.2 to 1.0 μm) α-Al_2O_3 powder.[†] The average diameter measured by an X-ray absorption/sedimentation technique[‡] was 0.37 μm. The average surface area as measured by standard BET N_2 adsorptions[§] was 5.9 m^2/g.

The polyelectrolyte studied was the Na^+ salt of poly(methacrylic acid) with an average molecular weight of 15 000.[¶] The PMAA-Na structure and dissociation reaction shown below illustrate that the functional groups are carboxylic acid groups that can be COOH or dissociated to COO^-. The PMAA-Na structure is



$$\left[-\underset{\underset{\displaystyle Na^+}{\displaystyle COO^-}}{\overset{CH_3}{C}}-CH_2-\underset{\underset{\displaystyle Na^+}{\displaystyle COO^-}}{\overset{CH_3}{C}}-CH_2-\underset{\underset{\displaystyle Na^+}{\displaystyle COO^-}}{\overset{CH_3}{C}}-CH_2-\right]_n$$

For each acid group

$$\text{A-COOH} + H_2O \longleftrightarrow \text{A-COO}^- + H_3O^+$$

$$Q = \frac{(\text{A-COO}^-)(H_3O^+)}{(\text{A-COOH})}$$

$$pQ = -\log Q = \text{pH} - \log\left(\frac{\alpha}{1-\alpha}\right)$$

where α is the fraction of dissociated acid groups.

The water used was distilled and deionized. The pH was adjusted with standardized analytical-grade HCl and NaOH solutions (0.1*N* to 1.0*N*). Analytical-grade NaCl was used to adjust the ionic strength as desired.

(2) Experimental Methods

(A) Potentiometric Titrations: To measure both the fraction

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[*] Member, the American Ceramic Society.

[*] Operated by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy.

[†] AKP-30, Sumitomo Chemical America, Inc., New York, NY.

[‡] Sedigraph 5000, Micromeritics, Norcross, GA.

[§] Quantasorb, Quantachrome Co., Syosset, NY.

[¶] Polysciences, Inc., Pittsburgh, PA.

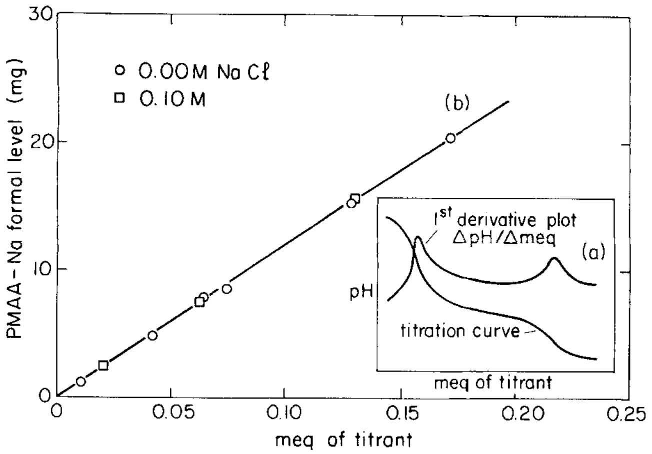

Fig. 1. (*A*) Typical titration curve for PMAA-Na and its corresponding first-derivative plot. (*B*) Linear relationship between the amount of PMAA-Na titrated and the mole equivalent of titrant corresponding to the distance between the peaks in (*A*).

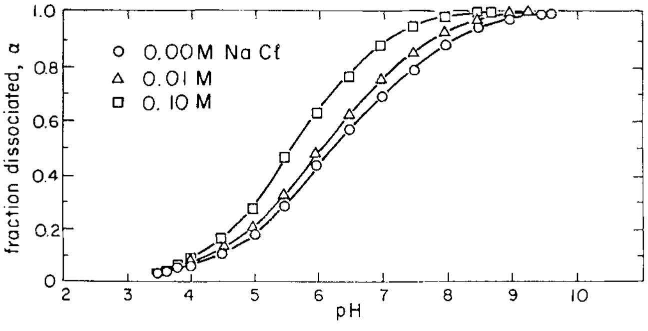

Fig. 2. Fraction of acid groups dissociated versus pH as a function of salt concentration for PMAA-Na salt (molecular weight of 15 000).

of dissociated COOH groups (α) versus pH for PMAA-Na and the surface charge versus pH for Al_2O_3, potentiometric titrations of the control electrolyte solutions were compared to titrations of the polymer solutions and oxide suspensions.[**]

This procedure of using potentiometric titrations to determine polymer behavior and solid-surface chemistry is clearly outlined by Arnold and Overbeek[5] and by Hunter.[6] Titrations were completed on a blank electrolyte solution and a corresponding polyelectrolyte solution or suspension containing a known amount of sample. The difference between the amounts of titrant added to the blank solution and the sample at a specified pH corresponds to the amount of titrant that reacted with the sample. With this information, both the fraction of functional groups dissociated on polyelectrolytes and the surface charge on ceramic powders can be easily calculated.[5,6]

The titrations were completed in a N_2 atmosphere on 40-mL samples containing known but small volumes of PMAA-Na (<0.1 g) and Al_2O_3 (<2 vol%). When desired, NaCl solutions were used to adjust the ionic strength. Prior to titration, the Al_2O_3 powder was cleaned to remove soluble ions using Soxhlet extraction[7] with freshly distilled water.

(B) Adsorption Isotherms: The adsorption of PMAA-Na on the alumina was evaluated using the automatic titration unit in the first-derivative titration mode. Suspensions of 20 vol% Al_2O_3 were prepared with various amounts of PMAA-Na at various pH values. While the Al_2O_3 was being added, the pH was constantly monitored and adjusted so that it was always within 0.2 pH unit of the desired pH value. After mixing, the samples were ultrasonicated for approximately 1 min at 50 W and the pH was measured and adjusted again if necessary. The samples were then put into a gentle mechanical shaker for approximately 24 h and then centrifuged for 45 min at 2000 rpm. A portion of the supernatant was then analyzed by first-derivative titration to determine the amount of PMAA-Na remaining in solution. Figure 1(*A*) shows the shape of a typical PMAA-Na titration curve and its corresponding first-derivative plot. The distance between peaks represents the amount of titrant required to reach the end point and depends linearly on the amount of PMAA-Na titrated as shown in Fig. 1(*B*). This relationship was therefore used to determine the amount of PMAA-Na remaining in solution after adsorption: A known volume of the supernatant was diluted with water to approximately 40 mL. This solution was then sealed in the titration cell and the pH was adjusted to 9.8, while the sample chamber was subjected to N_2 bubbling. The pH adjustment to 9.8 ensured that any PMAA-Na would be fully dissociated. This is discussed fully below. The first-derivative titrations were then conducted with 0.5*N* HCl and the distance between peaks recorded. Standards were prepared to establish Fig. 1(*B*) and this calibration was used to determine adsorption behavior of PMAA-Na. Background salt did not induce significant deviation in this calibration.

(C) Settling and Zeta-Potential Experiments: Settling experiments were done using 2 vol% Al_2O_3 suspensions. Various amounts of PMAA-Na were added to the suspensions which were then ultrasonicated and stirred for at least 4 h. Seventy milliliters of each suspension was then poured into graduated cylinders, and, after several days, the final sedimentation cake heights were recorded.

Electrophoretic mobility was measured[††] and used to calculate zeta potential according to Henry's equation.[8] These measurements can only be completed on very dilute suspensions. Therefore, the 2 vol% Al_2O_3 samples were centrifuged and the supernatant carefully decanted into a beaker; subsequently, a very minute amount of the sediment was remixed with the supernatant. The samples were ultrasonicated and stirred for 15 min prior to the measurements to ensure that only the mobility of the single particles was measured. At least 10 measurements were completed in each direction for each sample to ensure accuracy.

(D) Viscosity Measurements: Viscosity of the suspensions was measured using a rotary viscometer[‡‡] equipped with a recorder and a small sample chamber so that only 8-mL samples were necessary for each measurement.

III. Results and Discussion

(1) Chemistry of PMAA-Na and the Surface of α-Al_2O_3

The Na^+ salt of poly(methacrylic acid), with an average molecular weight of 15 000, has approximately 138 available carboxylic acid sites or functional groups per molecule. Depending on the solvent conditions (i.e., pH and ionic strength), the fraction of functional groups which are dissociated (i.e., COO^-) and those which are nondissociated (i.e., COOH) will vary. As the fraction dissociated (α) increases from ~0 to ~1.0, the polymer charge varies from relatively neutral to highly negative. Therefore, the behavior of the polymer in solution also depends on the solvent conditions. Figure 2 shows the fraction of dissociated acid groups as a function of pH and background NaCl concentration. As the pH and salt concentration increase, the extent of dissociation and negative charge of the polymer increase.

Figure 2 shows that at pH values ≥ 8.5 the PMAA-Na is negative and saturated with α approaching 1. In this condition, experimental evidence shows that the free polyelectrolyte is in the form of relatively large expanded random coils (~100 Å (~10 nm)) in

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[**] Radiometer TRS822, Radiometer, Copenhagen, Denmark.

[††] Micro-Particle Electrophoresis Apparatus Mark II, Rank Brothers, Bottisham, England.

[‡‡] Digital Viscometer, Model RVTD, Brookfield Engineering Laboratories, Inc., Stoughton, MA.

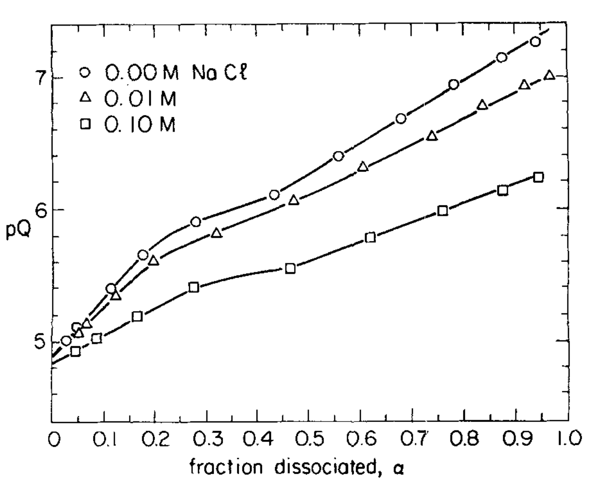

Fig. 3. p*Q* versus the fraction dissociated as a function of salt concentration for PMAA-Na salt (molecular weight of 15 000).

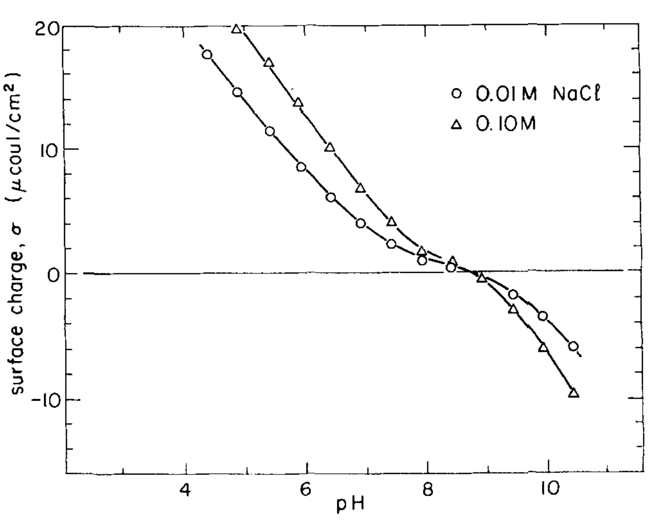

Fig. 4. Relative surface charge versus pH for the α-Al_2O_3 powder.

solution.[5] This configuration results from electrostatic repulsion between the negatively charged surface sites. As pH is decreased, the number of negatively charged sites also continually decreases until the polyelectrolyte is effectively neutral near pH 3.4 and α approaches zero. In this condition the polyelectrolyte chains approach insolubility and form relatively small coils (~30 Å (~3 nm)) or clumps.[5]

Because the titrations utilized only measure free hydronium ions and it is believed that in such low concentrations in water the A-COONa bonds are effectively fully dissociated, a plausible explanation for the role of salt concentration on the degree of dissociation is as follows: The probability of COO^- groups being stable, surrounded by Na^+ counterions in close proximity, increases with increasing [NaCl] and therefore the probability of H_3O^+ ions reacting with available COO^- groups to form COOH decreases. Additionally, added salt decreases the thermodynamic activity of H_3O^+, shifting the equilibrium toward more dissociation as depicted above.

Using similar reasoning, this behavior explains why p*Q*, defined above, increases with increasing α and decreasing background salt concentrations (Fig. 3). p*Q* is the effective dissociation reaction constant. For a polyacid such as PMAA, p*Q* varies for each acid site, depends on the local environment, and increases as each successive acid group dissociates. This situation occurs because increased electrostatic interactions between negative sites on the polymer make dissociation of neighboring sites more difficult. Since increased salt concentration promotes electrostatic shielding and makes dissociation less difficult, p*Q* decreases. An interesting note is that extrapolation of p*Q* values to $\alpha = 0$ yields 4.86. This value is consistent with those for simple organic acids which only have one acid group. Both the p*Q* and α behavior are in agreement with the PMAA titration results of Arnold and Overbeek.[5]

Figure 4 shows the charge density (σ) on the surface of the Al_2O_3 particles as a function of pH. At every pH, there is a large number of positive, neutral, and negative sites. The σ value gives the net charge density. At the zero point of charge (zpc), the number of positive sites equals the number of negative sites and the net charge equals zero. For our sample of α-Al_2O_3, the zpc is at approximately pH 8.7. Both σ values and the zpc are in very close agreement to that of Hasz.[9]

Finally, a comparison of Fig. 4 with Fig. 2 indicates that there should be a great deal of electrostatic attraction between the negatively charged polymer and the positively charged Al_2O_3, particularly in the pH range from 3.5 to 8.7. This relationship will be discussed further in the next section.

(2) Adsorption of PMAA-Na on α-Al_2O_3

To clarify the following discussion the initial polyelectrolyte added to the α-Al_2O_3 suspensions is in the form of a true solution of PMAA-Na with the PMAA and Na portions considered to be fully dissociated. However, for adsorption considerations the PMAA portion of the molecules is of primary importance and will be described as such.

Figure 5 shows adsorption at various pH values, plotted as milligrams of PMAA adsorbed per square meter of surface area of Al_2O_3 versus the initial amount of PMAA-Na added (on a dry

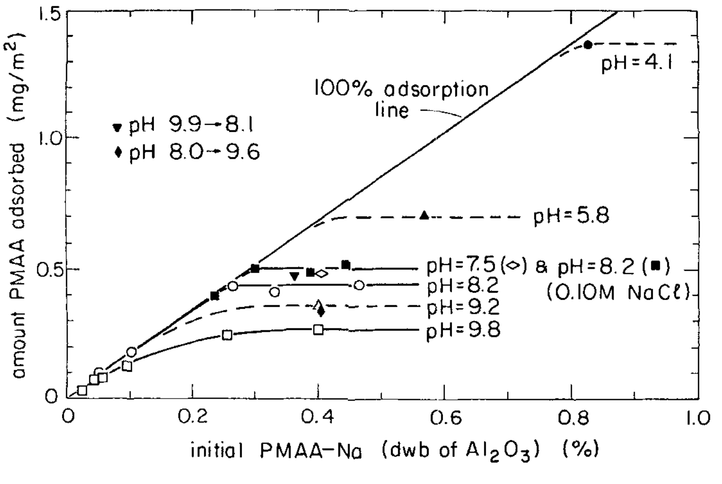

Fig. 5. Amount of PMAA salt adsorbed on α-Al_2O_3 as a function of the initial amount of PMAA-Na added.

weight of Al_2O_3 basis). The solid diagonal line represents the adsorption behavior that would occur if 100% of the PMAA added were to adsorb. Though this plot is not of the usual form for adsorption data, its utility in ceramic processing will become evident.

It is clearly shown that the amount adsorbed increases greatly with decreasing pH. This behavior agrees with the recent polyelectrolyte adsorption theory developed by Van der Schee *et al.*[10,11] For pH values above the zpc, $\alpha \approx 1$ and the negatively charged sites on the polyelectrolyte chains tend to repel each other. This repulsion suppresses the formation of loops in the adsorbed conformation. Consequently, the polyelectrolyte chains adsorb in a relatively flat conformation with each chain apparently covering a relatively large amount of surface area. Note that polyelectrolyte tails can still extend into solution even though the formation of loops is inhibited. The adsorption values for polyelectrolytes in this configuration are on the order of a few tenths of a milligram per square meter. As the pH is decreased and α approaches zero (Fig. 2), the polyelectrolyte chains become uncharged and the formation of loops in the adsorbed configurations is, in principle, enhanced. Thus, the projected surface area per adsorbed chain is relatively small, and more adsorbed chains are required to establish a saturated monolayer. Commonly measured values for this type of adsorption are a few milligrams per square meter which is in agreement with the experimental results.[12]

Figure 5 also shows a difference between the adsorption behavior above the zpc and below the zpc. For pH 9.8, there is a gradual attainment of the adsorption plateau. In constrast, for systems at pH 8.2 and less, the adsorption plateau adsorption is reached without any appreciable PMAA remaining in solution. Therefore, it is concluded that for pH values near and more acidic than the zpc, the adsorption behavior is of the high-affinity type. Practically all of the PMAA which is added adsorbs on the surface and the data follow the 100% line until a saturation plateau level is reached. Only beyond this limit does nonadsorbed PMAA become appreciably present in solution. This observation of high-affinity-type adsorption is also predicted by the adsorption theory of Van der Schee *et al.* When a negative or partly negative polyelectrolyte adsorbs on a *net* positively charged surface. This situation induces an added electrostatic influence on adsorption.[10,11] Because of similar net charges above the zpc, a barrier for adsorption increasingly develops. Therefore, in order to adsorb PMAA, there has to exist a corresponding equilibrium concentration of PMAA in solution. Adsorption in this region is still controlled by the minority of positive surface sites, even though the *net* surface charge is negative.

Figure 5 also shows that the presence of background salt can slightly increase adsorption. This occurs because the background salt has an electrostatic shielding effect between negatively charged sites on the PMAA thereby causing the chains to behave more like uncharged polymers and enhancing the development of loops. This type of behavior is commonly observed in many systems and agrees with recent concepts on adsorption.[10] It should be noted that, even with 0.1*M* NaCl concentrations, stable suspensions are achieved after saturation adsorption occurs.

Reversibility of adsorption is indicated by the ▼ and ● points on Fig. 5. Under these conditions, the suspensions were prepared at the initial pH values indicated and were shaken for 4 h. The suspensions were then adjusted to desired final pH values and were shaken for at least 20 h prior to analysis. The system, which is initially at pH 9.9 and then adjusted to pH 8.1, adsorbs a final amount equivalent to that obtained when the initial pH is 8.1. This correspondence might be expected because there is appreciable nonadsorbed PMAA in solution at pH 9.9 which could be easily adsorbed once the pH is lowered. A change in the configuration of the adsorbed PMAA may occur, but thus far no observable changes in the suspension behavior can be related to such changes. On the other hand, when the initial pH is 8.0 and then is adjusted to 9.6, complete reversibility is not observed, as only a fraction of PMAA desorbs. This behavior suggests that the PMAA is relatively strongly held on the Al_2O_3 surface. It also possibly indicates that with sufficiently extended times, most of the PMAA might desorb, at least for pH values near and above the zpc.

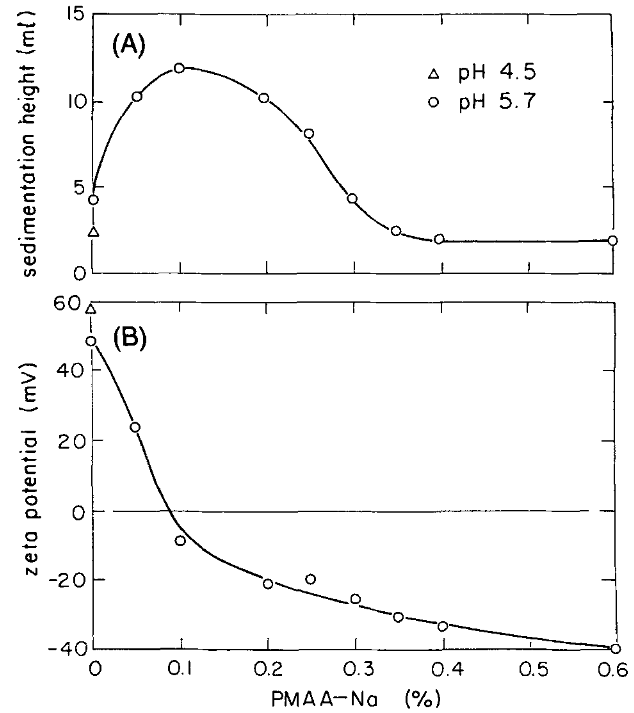

Fig. 6. (*A*) Sedimentation height and (*B*) zeta potential versus percent of PMAA-Na for 2 vol% suspensions of α-Al_2O_3.

(3) *Consolidated State*

The effect of incomplete adsorption and flocculation on the consolidated state was determined by sedimentation and centrifugation experiments. Figure 6(*A*) shows that trace amounts of PMAA-Na (<0.25%) induce flocculation and large sedimentation volumes. This results because the binding energy between the particles is high and the particle clusters that form during consolidation behave as rigid flow units and do not pack densely.[13] In contrast, at concentrations of approximately 0.35% to 0.50% PMAA-Na, the binding energy between particles is low and the particle clusters display a relatively denser packing structure.[13]

These data also correlate with the zeta potential determinations. Figure 6(*B*) shows that with increasing polymer concentration, the zeta potential decreases to zero and then reverses sign. Above 0.5% polymer, the zeta potential approaches a nearly constant value of −40 mV. This value reflects the saturated monolayer of polyelectrolyte on Al_2O_3.

It can be further concluded from Figs. 6(*A*) and (*B*) that small additions of PMAA-Na (e.g., <0.1%) neutralize charge and induce subsequent flocculation. In this regime, flocculation is mainly due to electrostatic patch model flocculation. This type of flocculation takes place because negatively charged patches due to the adsorbed polyelectrolyte are attracted to positively charged patches of surface on other particles. When the molecular weight is relatively low, maximum flocculation occurs when the zeta potential is approximately zero or even still slightly positive. This type of behavior is discussed by Bleier and Goddard.[14] In the range from 0.1% to 0.3% PMAA-Na, flocculation is due to a combination of two effects: the zeta potential is relatively low in magnitude and incomplete adsorption results in polymer bridging where two or more particles can mutually adsorb polymer chains.

It can also be concluded that with plateau adsorption coverage of PMAA, more efficient consolidation results. Upon settling, pure Al_2O_3 (0% polyelectrolyte) shows a larger sediment volume than the system with 0.4% polyelectrolyte added even though the zeta potentials are +48 and −33 mV, respectively. The stabilities determined by settling rates and sedimentation heights do not appear to be equal until zeta potentials of ≥58 mV are reached for the pure

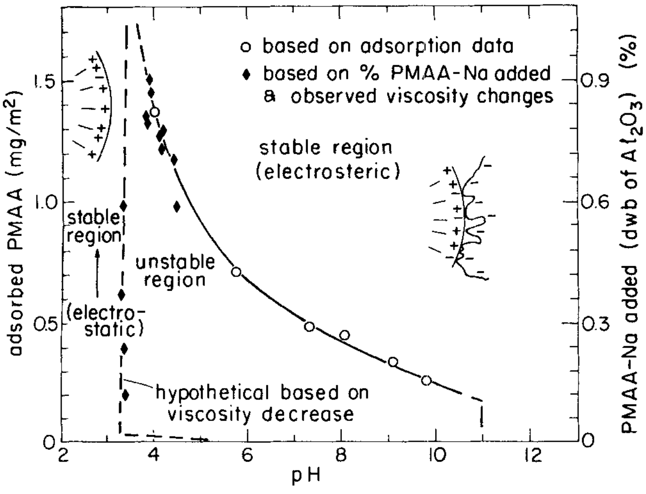

Fig. 7. Colloidal stability map of α-Al_2O_3 (20 vol%) suspensions as a function of adsorbed PMAA and pH.

Table I. Rheology Data at Various pH's*

pH	Viscosity† ($\times 10^{-3}$ Pa·s)
5.2	1650
7.4	<10
8.7	<10
9.3	<10
9.8	<10
10.2	<10

*20 vol% α-Al_2O_3 suspensions with 0.312% (dwb) of PMAA-Na (15 000 mol wt).
†At 10 rpm.

Al_2O_3 suspensions. This trend means that the increased stability and dispersion of the 0.4% polymer system may be due to a steric stabilization interaction in combination with the electrostatic repulsion. These mechanisms together can be termed electrosteric stabilization.

Some preliminary conclusions can be made from these results: Only very minute amounts of PMAA-Na are necessary to flocculate Al_2O_3 suspensions; a critical amount of PMAA-Na is needed before stabilization occurs; and PMAA-Na does indeed provide an enhanced stabilization effect.

(4) Stability Map for PMAA-Na/α-Al_2O_3 System

With the above information and the adsorption data in Fig. 5, a stability map can be constructed. Figure 7 is a plot of the amount of PMAA adsorbed at the plateau levels versus pH. In other words, for any pH near and below the zpc, it is a measure of the amount of PMAA which must be adsorbed to achieve a stable suspension. Regions below the curve are unstable and show an onset to flocculation. Regions near and slightly above the curve are stable and dispersed. Regions further above the stability curve have appreciable amounts of free polyelectrolyte in solution and induce stabilization complications that will not be discussed in this paper. However, the effects of free polyelectrolyte have been examined in detail elsewhere.[15,16] The reason for the assumed steep decrease in adsorption at pH 3.3 is observed decreases in viscosity. For example, as pH is decreased on samples which are initially stable, the viscosity noticeably increases when crossing the stability/instability boundary region. This is expected because at those lower pH values, more PMAA is needed to maintain a stable suspension and the subject suspensions are below that critical level. This process is the same as moving to the left from a stable region on Fig. 7 and entering the unstable region. Once the pH is decreased further to 3.3, deflocculation reoccurs and viscosity sharply decreases and approaches that of a system stabilized at pH 3.3 without any PMAA present. Because at pH 3.3 the suspension is stable without the presence of PMAA due solely to electrostatic interactions, it is believed that there is a combination of two possible mechanisms for the observed restabilization of Al_2O_3 below pH 3.3 in the presence of PMAA. One explanation is that below pH 3.3 the PMAA sufficiently desorbs because this is also the pH at which the PMAA loses its negative charge, and its configuration and electrical state approach those of a neutral polymer with a greatly diminished driving force for adsorption (Fig. 2); it may even approach its solubility limit. Alternatively, some PMAA may still be adsorbed, but the effectively neutral polymer layer may be thin enough that the electric double layer (formed by the highly positive Al_2O_3 surface) may extend past the polymer layer. In this way, electrostatic stabilization due to electric double layer interactions can still occur.

Table I illustrates the transition from stability to instability based on viscosity measurements. A series of samples with 0.312% PMAA was prepared at various pH values. Viscosities of samples above pH 7 were $<10^{-2}$ Pa·s while the viscosity of the sample at pH 5.2 was more than 2 orders of magnitude greater, indicating flocculation. This is in agreement with Fig. 7, which shows a stability/instability transition at pH ~7 for 0.312% PMAA.

IV. Conclusions

(1) The adsorption behavior of the Na salt of poly(methacrylic acid) on alumina depends on solvent conditions and the charge characteristics of the PMAA-Na and the Al_2O_3 surface: As pH is decreased, the adsorption of PMAA increases until insolubility and charge neutralization of the PMAA-Na is approached. For pH values near and below the zero point of charge (zpc) for Al_2O_3, there is an added electrostatic attractive potential for adsorption which results in a high-affinity-type adsorption behavior.

(2) For pH values near and below the zpc, PMAA adsorbs and may induce flocculation until an adsorption saturation limit is reached and the binding energy between particles is reduced below a critical level.

(3) Once saturation adsorption occurs and stability is achieved, the PMAA-induced stabilization exhibits an enhanced stability compared to suspensions stabilized electrostatically without the polyelectrolyte.

(4) The stability map introduced here is a useful processing tool for tailoring suspensions with varying amounts of polyelectrolyte, depending on the desired properties. For instance, if higher concentrations of polyelectrolyte are desired, perhaps for high mechanical strength in the consolidated state, acidic conditions would be recommended. However, if dispersion is ultimately important and the effects of the adsorbed polymer are not desired, basic conditions would be more suitable. The knowledge gained from the stability map is necessary to predict the amount of polyelectrolyte necessary to stabilize aqueous alumina suspensions at various pH's for any known surface area and well-defined zpc. And, the use for such stability maps to help control a variety of ceramic systems stabilized with polymers appears to have a great deal of potential.

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Thermal Diffusivity of Partially and Fully Stabilized (Yttria) Zirconia Single Crystals

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Laser flash measurements of thermal diffusivity of ZrO_2 single crystals partially and fully stabilized with Y_2O_3 were compared with measurements for polycrystalline cubic ZrO_2, and single crystals and polycrystals of Al_2O_3 and $MgAl_2O_4$. In general, the thermal diffusivities of the ZrO_2 materials examined initially decrease with increasing temperature, although significantly less than for the Al_2O_3 and $MgAl_2O_4$ materials. The diffusivity subsequently rises with increasing temperature for the single crystals of ZrO_2 but not for polycrystalline cubic ZrO_2, with this increase for ZrO_2 crystals occurring at much lower temperatures than for Al_2O_3 and $MgAl_2O_4$ crystals. As the ZrO_2 materials went from fully stabilized with 20 wt% Y_2O_3 to partially stabilized with 5 wt% Y_2O_3, the room-temperature diffusivity increased from 0.70×10^{-6} to 0.97×10^{-6} m^2/s. This indicated that the lattice defects, which increase with Y_2O_3 content, are more important sources of phonon scattering than are the precipitates which appear at lower Y_2O_3 compositions. On the other hand, at 1000°C the diffusivity of the fully cubic ZrO_2 crystals with 20 wt% Y_2O_3 was 1.10×10^{-6} m^2/s while that of the partially stabilized ZrO_2 crystals with 5 wt% Y_2O_3 was 1.05×10^{-6} m^2/s. The increased diffusivity at higher temperatures can be attributed to radiative heat transfer, with the lower relative diffusivity of the partially stabilized crystals resulting from photon scattering by the precipitate structures present.

I. Introduction

PARTIALLY stabilized ZrO_2 (PSZ) is of increasing interest for a variety of applications where its thermal diffusivity can be of importance as well as its strength and toughness.[1,2] For applications in heat engines or as thermal barrier coatings, the thermal diffusivity and conductivity become critical design parameters.[3] The zirconias of current interest range from fully stabilized cubic to partially stabilized materials, i.e, two-phased cubic plus tetragonal or fine-grained tetragonal ZrO_2. However, as the stabilizer content is reduced, the associated oxygen lattice defect population is also decreased.[4–6] The oxygen lattice defects, as well as impurities, second phases, grain-boundary phases, and phase boundaries, can be sources of phonon scattering which may affect the diffusivity. The thermal diffusivity or conductivity has been measured only on a limited range of polycrystalline materials[7,8] with different stabilizers and crystal phases; however, the nature of the stabilization effect on thermal diffusivity has not been examined.

At low temperatures, e.g., room temperature, where radiation effects can be neglected, the Debye expression for the thermal conductivity can be used to examine the thermal behavior of materials. The thermal conductivity, κ_{phonon}, can be expressed as $\kappa_{\text{phonon}} = C_p\rho vL/3$, which is a fundamental thermal transport property[9,10] and depends on the phonon mean free path, L, the specific heat, C_p, the density, ρ, and on the elastic wave veolcity, $v = [E/\rho]^{1/2}$, where E is Young's modulus. Generally, the temperature dependence of the thermal diffusivity, α, can be understood in terms of the various phonon scattering mechanisms which affect L. Lattice defects, phase and grain boundaries, the extent and character of which have different dependences on the type and amount of stabilizer additive, can be sources of phonon scattering mechanisms which will affect the diffusivity. Even for single crystals where grain boundaries are absent, the scattering mechanisms are important and complex because of the essentially opposite dependences of the lattice defects and the phase (precipitate) boundaries on stabilizer content. Therefore, an issue is whether the diffusivity is affected more by phonon scattering arising from the lattice defects or from the precipitate structures. At higher temperatures, where photon or radiative transport can become important, effects of photon scattering by precipitates in partially stabilized materials are now a consideration. The effects of stabilization and precipitate structures on the thermal diffusivity of

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