

Effect of poly(acrylic acid) and poly(vinyl alcohol) on the solubility of colloidal BaTiO₃ in an aqueous medium

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The influence of poly(acrylic acid) (PAA) and poly(vinyl alcohol) (PVA) on Ba dissolution from the BaTiO₃-aqueous solution interface was investigated. Incongruent dissolution of Ba impacts the colloidal stability, microstructure, and electrical properties of BaTiO₃ and related perovskite dielectric materials used in the manufacture of ceramic capacitors. The solubility characteristics of BaTiO₃ were influenced significantly by the presence of PAA and PVA. PAA, which forms weak monodentate complexes with Ba²⁺, acted as both a passivating and a sequestering agent, depending on pH. Both PAA and PVA provided some degree of passivation in the acidic pH region. Above pH 8, where BaTiO₃ solubility decreases sharply, PVA had a moderate passivating effect, whereas solubility was enhanced by PAA with a positive linear dependence on concentration. The adsorptive and electrokinetic behavior of colloidal BaTiO₃ with respect to PAA and PVA are correlated with the observed passivating and sequestering properties of these polymers.

I. INTRODUCTION

Barium titanate is used extensively as a starting material in the fabrication of Y5V and X7R multilayer ceramic capacitors (MLCCs) because of its excellent dielectric properties.¹⁻³ In general, the dielectric layers in MLCCs are fabricated by the doctor blade tape casting method.⁴ Although solvent-based ceramic slurries have been traditionally used, there has been a recent push toward aqueous-based tape casting for cost-related and environmental benefits. However, a critical difficulty associated with aqueous-based systems is the incongruent dissolution of BaTiO₃ and the resulting accumulation of Ba²⁺ in solution; this effect is accelerated in acidic media due to thermodynamic instabilities.⁵⁻⁹ As recent investigations have shown,^{10,11} the dispersion stability of colloidal BaTiO₃ is closely tied to changes in the surface chemistry that result from leaching of Ba²⁺ ions. Dispersion stability has a critical impact on particle packing,¹² which in turn influences the microstructure and electrical properties of the sintered dielectric layer.¹³ An increase in dielectric layer permittivity of MLCCs can be achieved by decreasing the sheet thickness and increasing the stacking layers. As the particle size is reduced to

achieve thinner sheets, agglomeration, which can degrade packing density, becomes a considerable issue in wet processing.

In addition, the dielectric and microstructural properties of BaTiO₃ are very sensitive to stoichiometry, and small deviations may cause significant deterioration or enhancement of the dielectric response. Ti excess has been reported to cause exaggerated grain growth and a reduction in permittivity due to the formation of a liquid phase^{14,15} but to promote the overall densification process.⁹ On the other hand, Ba excess has been reported to increase permittivity and impact ferroelectric properties.¹⁴ Carbonate contamination, a ubiquitous problem in BaTiO₃ processing, has been linked to retarded densification and surface defects¹⁶ and to other deleterious effects resulting from internal pressure created by CO₂ release.¹⁵ Nonstoichiometry can also be induced by leaching of Ba from the BaTiO₃ surface region upon contact with an aqueous phase,^{9,17} thus leading to further difficulties in controlling the final dielectric properties. Understanding dispersion stability and passivation at the BaTiO₃-aqueous solution interface is therefore essential for establishing predictable and reliable aqueous-based tape casting.

In this context, the influence of soluble polymers on the dissolution of BaTiO₃ is of particular interest. Polycarboxylates, such as poly(acrylic acid) (PAA) or poly(methacrylic acid) (PMAA), and nonionic polymers, such as poly(vinyl alcohol) (PVA), are commonly used in aqueous-based processing as dispersing agents and binders, respectively. A number of previous studies have examined the interaction between polycarboxylates and BaTiO₃ in aqueous systems;^{18–31} with only one exception,²⁸ all studies involved PAA and/or PMAA. In general, these studies focused on the adsorptive and dispersive properties of the polymer with respect to BaTiO₃. Unfortunately, factors like macromolecular chain length (i.e., relative molar mass), pH, ionic strength, equilibration time, temperature, and solids loading varied widely among these investigations, and in some instances critical parameters were not controlled or described adequately. Nevertheless, several clear conclusions can be drawn from this prior work: (i) Polycarboxylate adsorption increases with decreasing pH and increasing salt concentration. (ii) Longer chain-length molecules are adsorbed preferentially. (iii) The dosage needed to stabilize BaTiO₃ decreases with increasing pH. (iv) Saturation adsorption results in charge reversal and a negative zeta potential over the practical pH range. Although a number of authors raised the issue of BaTiO₃ dissolution and the possible influence of Ba²⁺ ions on adsorption, of these only three studies actually examined the effect of Ba²⁺ on polycarboxylate adsorption or surface interactions,^{24,29,30} wherein it was found that the presence of Ba²⁺ enhances adsorption and, in sufficient concentrations, leads to flocculation of the polymer. More importantly, only two studies have directly measured the effect of the polycarboxylate on BaTiO₃ dissolution,^{23,28} both finding a significant passivation effect at basic pH values. However, these last two studies were limited in scope and did not examine the dependency of passivation/dissolution on either pH or polycarboxylate concentration.

By contrast, remarkably few published studies have concerned PVA in the aqueous BaTiO₃ system.^{19,31,32} What has been reported focused primarily on adsorption phenomena in basic media, including competitive effects in mixed PVA–PAA systems, without consideration of BaTiO₃ dissolution as a mitigating factor in adsorption (or, conversely, the potential effect of PVA adsorption on dissolution).

Presently, we report on the separate interactions of PAA and PVA at the BaTiO₃-aqueous solution interface and their impact on leaching of Ba²⁺ ions. We measured the electrokinetic response, polymer adsorption, and dissolved Ba concentration, as a function of both pH and polymer dosage for each species. The results are correlated to provide an understanding of the underlying mechanisms of interaction with BaTiO₃ and the factors that influence passivating and sequestering behavior in this system.

II. MATERIALS AND METHODS

Hydrothermal BaTiO₃ powder (BT-04, Sakai Chemical Industry Co. Ltd., Sakai City, Japan) was used in this investigation. The specific surface area provided by the manufacturer was 3.10 ± 0.05 m²/g; this value was used to normalize adsorption on a per unit surface area basis. Analytical grade chemicals (HCl, NaOH, and NaNO₃) were used to adjust the suspension pH and ionic strength in suspensions. Organic additives, PAA (*M_r* = 5000) and PVA (98 mol% hydrolyzed, *M_r* = 78,000) were obtained from Polysciences (Warrington, PA). Physical and chemical data for each compound were provided by the manufacturer. PAA is a moderately weak polyacid that dissociates to form anionic carboxylate functional groups. PVA, by contrast, is a nonionic polymer (at normal pH values) containing alcoholic hydroxyl groups and 2 mol% residual acetate units. PAA and PVA stock solutions were prepared by dissolving in deionized water. All suspensions were prepared by mixing BaTiO₃ powder with diluted polymer solutions containing the required amount of PAA or PVA.

Adsorption isotherms for PAA and PVA on BaTiO₃ as a function of pH were determined by the solution depletion method³³ using a total organic carbon (TOC) analyzer (ASI-5000A, Shimadzu, Kyoto, Japan), in which a known amount of liquid sample is injected and combusted at 680 °C. Carbon content is then measured as CO₂ using a nondispersive infrared detector that has been calibrated against potassium biphthalate TOC standards prepared gravimetrically. Adsorption isotherms were measured at a solid phase volume fraction of 5%. Adsorption was calculated from the difference between the known (total) polymer concentration and the measured concentration that remained in the supernatant after equilibrating by magnetic stirring at 23 ± 1 °C for 12 h. The pH was preadjusted to obtain postaging nominal pH values of 3, 6, and 9; aging affected a systematic increase in pH over time. Each sample injection was analyzed three times for TOC and averaged. In addition, periodic replicate injections were performed. Measured values were corrected for background TOC determined from a powder-solution blank.

To characterize the electrokinetic response of BaTiO₃ suspensions, dynamic mobility was measured as a function of pH using an ESA 9800 analyzer (Matec Applied Sciences, Hopkinton, MA). Details of this technique, its application to ceramic systems, and the estimated measurement precision have been given previously.^{34,35} Suspensions containing a solid-phase volume fraction of 2% were dispersed by ultrasonic treatment for 3 min using a submersible titanium horn and then equilibrated for 12 h prior to electrokinetic measurements. All titrations were performed by the addition of acid to initially basic suspensions.

Dissolved Ba concentration was determined at a solid phase volume fraction of 5% using inductively coupled plasma-atomic emission spectroscopy (ICP-AES, ICPS-1000IV, Shimadzu, Kyoto, Japan). For each suspension, the pH was preadjusted considering the aging effect, and then the sample was equilibrated by magnetic stirring at room temperature for 12 h prior to analysis. Following equilibration, samples were centrifuged at 15,000 rpm for 30 min. Supernatants were extracted and clarified with a 0.2- μm Acrodisc filter cartridge (Gelman Sciences, Ann Arbor, MI). Three replicate ICP-AES analyses were performed for each clarified supernatant.

III. RESULTS AND DISCUSSION

A. Adsorption isotherms for PAA and PVA

The pH dependence of adsorption isotherms for PAA on BaTiO₃ is shown in Fig. 1. The Langmuir adsorption equation appeared to overestimate the plateau value, and so isotherms were fit instead using a simple 2-parameter exponent relationship of the form $\Gamma = a(1 - b^x)$, where Γ is the surface-area-normalized adsorbed amount, a is the adsorption plateau (Γ_{max}), b is a scaling constant, and x is the residual concentration. As expected, Γ_{max} increases significantly with decreasing pH, rising from 0.22 mg/m² at pH 9 to nearly 1 mg/m² at pH 3 (Table I). A similar trend was reported previously for PAA of the same relative molar mass onto colloidal Si₃N₄,³⁶ this is a generally reported trend regardless of the substrate material. Although the trends are similar, a comparison of Γ_{max} for PAA on Si₃N₄ and on BaTiO₃ (at pH 3) shows that the latter substrate adsorbs roughly fourfold more polymer.

Figure 2 shows the adsorption isotherms for PVA onto BaTiO₃ at pH 3, 6, and 9. The results show a clear trend of increasing adsorption with decreasing pH, similar to PAA. However, Γ_{max} for PVA is much lower (about 1/3)

relative to PAA at the two lower pH values, and the dependence of adsorption on pH is much weaker for PVA; the spread in plateau adsorption values from pH 3 to pH 9 (approximately 0.1 mg/m² for PVA compared to approximately 0.7 mg/m² for PAA) reflects strength of pH dependence.

The different adsorptive behaviors of PAA and PVA on BaTiO₃ can be attributed to the different functional groups on each polymer. For PAA, the acidic carboxyl group is characterized by a pH-dependent ionization and the ability to exchange with surface hydroxyls, bonding with the underlying metal ion in solid oxides like BaTiO₃. With binding of multiple carboxyl groups on the surface, this leads to irreversible high-affinity adsorption with a strong pH dependence.³⁶

The strong adsorption of PAA at pH 3 is the result of two coupled effects: (i) With the near-zero degree of ionization (α) at pH 3, repulsive interactions between adjacent carboxyl sites are eliminated, and a coiled conformation permits a denser packing on the particle surface.³⁶⁻³⁸ (ii) The low α value also leads to a reduced solvency, forcing the polymer onto the surface.^{36,37} Therefore, a general trend observed for PAA adsorption on oxide and nonoxide substrates alike is one of increasing adsorption with decreasing pH.

TABLE I. Relationship between PAA adsorption and passivation.^a

pH	Γ_{max}	[PAA] _{total} at 95% Γ_{max}	[PAA] _{resid} at 95% P_{max}	[PAA] _{total} 95% of P_{max}
3	0.88	3.6	2.7	4.2
6	0.61	4.9	4.2	3.8
9	0.22	no saturation	no passivation	no passivation

^aSubscripts refer to maximum (max), total of adsorbed and nonadsorbed (total), and nonadsorbed only (resid). Γ_{max} is the saturation adsorption determined from a fit of the experimental data, and P_{max} is the estimated point of maximum passivation as determined from the dissolution of Ba versus polymer concentration. All units are mg/m².

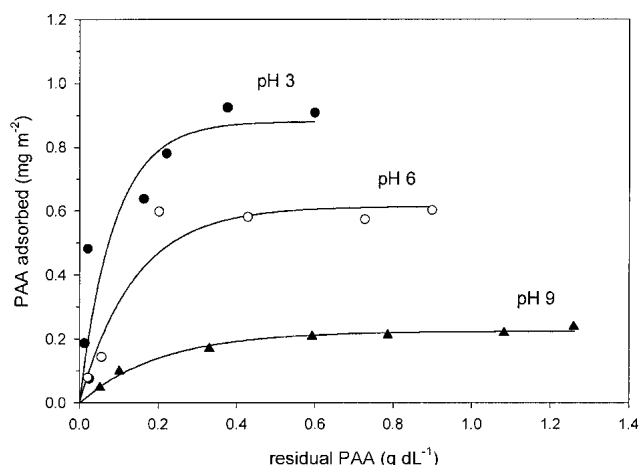


FIG. 1. Influence of pH on adsorption isotherm for PAA on BaTiO₃. Error bars (not shown) are smaller than the symbol size.

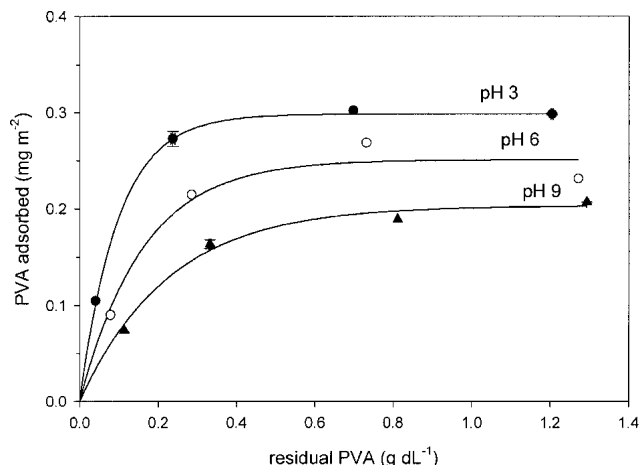


FIG. 2. Influence of pH on adsorption isotherm for PVA on BaTiO₃. Error bars indicate standard uncertainty of TOC analysis.

A contributory factor for PAA adsorption in acidic media may be coupled to the pH-dependent leaching of Ba²⁺ into solution. In general, an increase in ionic strength of the solution phase can lead to increased polyelectrolyte adsorption due to a reduction in solvency, even for inert (noncomplexing) monovalent counterions. However, the stronger the counterion association with the carboxylate group, the greater the screening effect on polyelectrolyte charge, and it is known that alkaline-earth cations bind to PAA via monodentate complexes with the COO⁻ ligands.^{39,40} This leads to a strong screening effect. For example, it has been shown that the addition of 5 mmol/l CaCl₂ boosts the uptake of PAA on titania threefold.⁴¹ Similarly, Li and Jean³¹ found that addition of BaCl₂ increased PAA adsorption on BaTiO₃ threefold at pH 7.5; the effect increased with increasing pH. They also found that addition of BaCl₂ to a PAA solution, at concentrations above 0.02 mol/l, caused the polyelectrolyte to flocculate. The adsorption and flocculation experiments taken together indicate a clear link between changes in PAA solvency and adsorption. Since, for BaTiO₃ in water, the concentration of dissolved Ba²⁺ generally increases with decreasing pH, a Ba²⁺-complex-mediated process is not inconsistent with the observed pH dependence of PAA adsorption and may work to further enhance the intrinsic loss of solvency that occurs with decreasing α values.

On the other hand, Blanco-Lopez *et al.*²⁴ found no observable effect on sediment density for BaTiO₃ suspensions, from pH 2 to pH 6, when BaCl₂ was added at levels up to a Ba:COOH ratio of 10:1, suggesting that Ba²⁺ may not significantly complex PAA in acidic media. An alternative explanation is that the effect of BaCl₂ addition is minimal in this case, because of the high Ba²⁺ load already present from dissolution of the solid phase, resulting in an already unstable suspension (sediment density was equally low in the absence or presence of polymer below pH 6). Above pH 6, the addition of BaCl₂ at the 10:1 ratio induced flocculation of otherwise stable suspensions; here the native Ba²⁺ load is reduced, and so the addition of BaCl₂ has a substantial effect. Although the authors speculate that the dispersive properties of PAA would be “blocked” by the addition of BaCl₂, they did not measure polymer adsorption and therefore the link between destabilization of BaTiO₃ suspensions and solvency-driven adsorption of PAA is not explicit in their work. Regardless, complexation is certainly weaker in acidic media due to competition with protons for the anionic carboxylate sites and is therefore of relatively less importance in terms of charge neutralization-induced adsorption of PAA.

At pH 9, BaTiO₃ exhibits lower, but still fairly significant uptake of PAA, with Γ_{\max} reaching 25% of its value at pH 3. As the pH increases, and PAA becomes increasingly deprotonated, it will uncoil and assume a stretched

conformation that occupies more surface area per molecule³⁸ and thus reduces the adsorbed amount. Offsetting this effect are two factors: (i) an increasingly attractive electrostatic interaction between anionic PAA (at pH 8, $\alpha > 0.8$)³⁶ and the positively charged BaTiO₃ surface; (ii) surface complex formation. Both of these factors increase in importance with increasing pH, up to about pH 10 for this particular powder (i.e., up to the pH_{iep}). The formation of a complex between the anionic carboxylate group of PAA and either adsorbed or lattice Ba²⁺ ions is promoted in basic media, because Ba remains largely surface bound and the apparent stability constant for the PAA–metal ion complex increases with α ,⁴⁰ which in turn increases with pH.³⁶ Complex formation also acts to stabilize the adsorbed conformation. Therefore, we predict that the Ba:Ti ratio at the surface will significantly impact adsorption of polycarboxylates like PAA. Similarly, any postsynthesis treatment that modifies this ratio will impact uptake. Above pH 10, PAA is fully ionized³⁶ and the surface of BaTiO₃ is negatively charged (see subsequent discussion of electrokinetic titrations). As a result, electrostatic repulsion will act as a barrier to adsorption and complex formation.

At pH 6, where PAA is approximately 40% dissociated,³⁶ adsorption is intermediate between pH 3 and pH 9, with a saturation limit of about 0.6 mg/m². The principal driving force for adsorption at this point is probably electrostatic attraction between the polar opposite polyelectrolyte and particle surface, although complex formation may also play a contributing role here if sufficient Ba ions remain bound to the solid surface (this is unlikely, because of the high solubility of BaTiO₃ at pH 6). Normally, polymer solvency would not be an issue at this pH, since the molecules carry a sufficient charge density to be hydrophilic and partially uncoiled. However, just as in the case at pH 3, the presence of a fairly significant amount of dissolved Ba²⁺ at pH 6 probably promotes some complex formation and screening, which would favor adsorption.

Isotherms for PAA at both pH 3 and pH 6 can be classified as high-affinity type, characterized by a steep initial uptake at low concentrations, while the isotherm at pH 9 clearly exhibits a more gradual approach to saturation. All three isotherms exhibit saturation (monolayer) adsorption.

In contrast to PAA, the interaction between neutral polyols and metal ions is very weak, and complex formation is generally not significant in aqueous solution.⁴² Only in very basic media, pH > 12, can PVA deprotonate to form a strong metal-binding ligand. As a result, the protonated hydroxyl groups on PVA (at pH values <12) presumably adsorb to the particle surface via relatively weak hydrogen bonds.^{33,43,44} The degree of hydrogen bonding is then a function of the density and nature of surface hydroxyl groups, which, for BaTiO₃, is

pH-dependent. We hypothesize that as Ba is lost from the surface with decreasing pH, leaving a hydrolyzable oxide-rich surface layer, the density of surface hydroxyls will increase, thereby facilitating hydrogen bonding with PVA. This would explain the weak pH dependence observed in Fig. 2. Similar pH trends have been reported for PVA adsorption on both Si₃N₄³³ and SiO₂,⁴⁴ but in each of these cases the primary adsorption sites were silanols (Si–OH) (and also siloxanes, Si–O–Si, in the case of SiO₂). For PVA adsorption on SiO₂, deprotonation of Si–OH with increasing pH has been proposed by Tadros⁴⁴ and others to explain the observed decrease in adsorption; only protonated sites can participate. This mechanism could also apply to PVA adsorption on BaTiO₃, if we assume that here the surface OH sites are primarily associated with Ti. On the basis of low pH_{iep} values reported for titania (pH 4–6), Ti–OH groups are relatively acidic (though more basic than silanols), and the majority of hydroxyl sites would therefore be dissociated at pH 9 and not able to form hydrogen bonds with PVA. In spite of the apparent similarity in the pH dependence for PVA adsorption on BaTiO₃ and SiO₂, and the weak interaction between neutral PVA and metal ions below pH 12, the re-adsorbed Ba²⁺ cannot be ruled out as a factor in the adsorption process for PVA. Although resolving this matter is beyond the scope of the present work, we can suggest that some careful diffuse reflectance infrared Fourier transform (DRIFT) or cylindrical internal reflectance-Fourier transform infrared (CIR-FTIR) experiments might shed further light on the nature of the adsorption mechanism for PVA on BaTiO₃.

B. Electrokinetic behavior

Figure 3 illustrates the effect of PAA on the electrokinetic behavior of BaTiO₃ as a function of pH. As previously reported,⁴ electrokinetic titrations of this powder in the absence of PAA and at moderate solids loadings do not exhibit a pH_{iep}. The particles therefore remain positively charged (positive dynamic mobility) over the entire experimental pH range. However, once the particles have been in contact with an acidic solution, the leaching of Ba results in a Ti-excess oxide-rich surface. Therefore, in acidic media the surface hydroxyls are predominantly associated with the tetravalent Ti cation, as previously stated, and the surface is characteristically acidic. If, for example, leached Ba²⁺ is removed following acid treatment, a relatively acidic pH_{iep} (approximately pH 5) is observed.¹¹

The presence of PAA shifts the titration curve toward more acidic pH values and results in the appearance of a well defined pH_{iep}. The pH_{iep} continues to shift in the acidic direction with increasing PAA concentration, confirming that the anionic functional group of PAA is specifically adsorbed on BaTiO₃. The adsorption of PAA imparts an increasingly negative potential to the

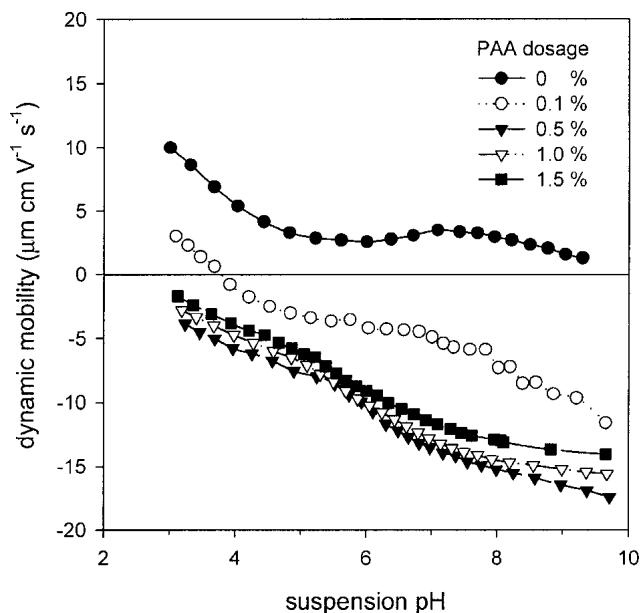


FIG. 3. Electrokinetic titration curves for BaTiO₃ as a function of PAA concentration (on a mass basis relative to BaTiO₃) and suspension pH.

particles, with a maximum effect occurring at a PAA dosage near 5 mg/g (1.6 mg/m²). Above this amount, polyelectrolyte simply accumulates in the bulk solution and contributes to screening of the particle surface charge with the attendant reduction in the absolute value of mobility. These results can be compared with the adsorption isotherms in Fig. 1 (Table I), which indicate that surface saturation of PAA is achieved at a total dosage (adsorbed + free) of about 4 mg/m² at pH 3.

For free PAA in solution, α approaches zero at pH 3.³⁶ Yet, results here indicate that at total polymer concentrations exceeding about 2–3 mg/g (approximately 0.7–1 mg/m²) PAA imparts a negative potential to BaTiO₃ over the entire experimental pH range. For a surface saturated with PAA, extrapolation of data in Fig. 3 yields a pH_{iep} just below pH 3. The charge reversal that occurs on BaTiO₃ at sufficiently high polymer concentrations is a consequence of the overcompensation of positive surface charge. This effect can be explained by consideration of two factors: (i) the specific (nonelectrostatic) contributions to the free energy of adsorption; (ii) enhancement of carboxyl acidity near the particle surface. The specificity of PAA adsorption arises from the chemical interaction of the carboxylate groups with surface metal ions to form surface complexes, a process that is analogous to solution phase complex formation between carboxyl ligands and dissolved metal ions.⁴⁰ This additional chemical contribution to the free energy of adsorption can lead to superequivalent adsorption and overcompensation of surface charge.⁴⁵ The second factor, enhanced carboxyl acidity, is a result of the electric field generated by the charged substrate. Using a lattice-based

self-consistent-field theory, Böhmer *et al.*⁴⁶ predicted the pK_a of weak-acid functional groups of adsorbed polyelectrolyte would increase when in close proximity to a positively charged surface. The enhancement of acidity leads to the accumulation of additional negative charge within the shear plane and suggests that PAA adsorption could produce a negative zeta potential at pH values well below the intrinsic pK_a .

Figure 4 shows the effect of PVA on the electrokinetic behavior of BaTiO₃. Although a general reduction in electrokinetic potential is observed over the entire pH range of the titration, a charge reversal does not occur as it does in the presence of PAA. This is consistent with previous work showing that adsorption of nonionic PVA will lower the electrokinetic potential of charged particles.³³ This phenomenon is largely physical in nature, resulting from the outward shift of the hydrodynamic shear plane away from the particle surface and is due to the hydrodynamically disruptive presence of the polymer chains at the interface. As a result, the largest impact is observed in the acidic pH range, where PVA adsorption (Fig. 2) is greatest. The lack of a pH_{iep} shift in the electrokinetic curves in the presence of PVA, coupled with the relatively weak adsorption and weak dependence of adsorption on pH, indicate that PVA interaction at the BaTiO₃-aqueous solution interface is neither covalent nor electrostatic in nature. Therefore, weak passivating behavior exhibited by PVA in acidic media at low polymer concentrations most likely derives from either the presence of a physical barrier (adsorbed layer of PVA) or some stabilizing effect due to weak hydrogen bonding

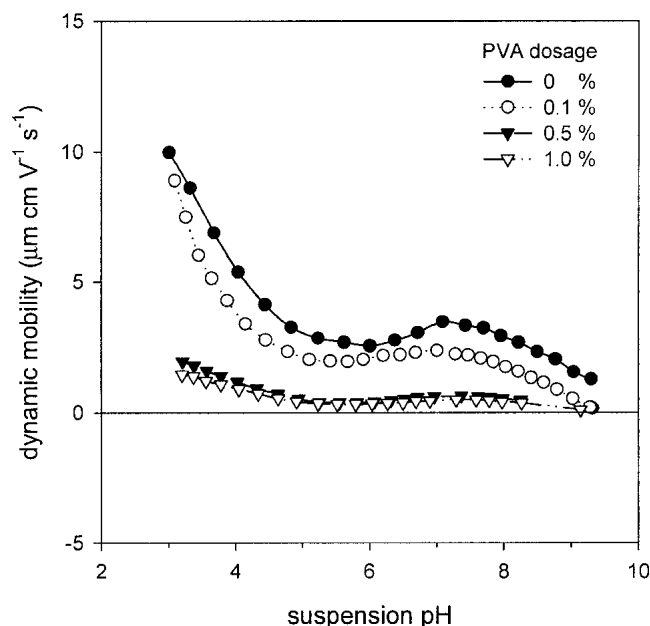


FIG. 4. Electrokinetic titration curves for BaTiO₃, as a function of PVA concentration (on a mass basis relative to BaTiO₃) and suspension pH.

by PVA hydroxyl groups at the BaTiO₃ surface. On the other hand, the effect of PVA on the position of the shear plane will undoubtedly impact colloidal stability to some degree.

C. Effect of PAA and PVA on Ba dissolution

The pH dependence of Ba dissolution in the presence of increasing PAA concentration is shown in Fig. 5. It is clear that PAA can behave as either a passivating agent or as a sequestering agent, depending on pH. At pH 8 and higher, where PAA is mostly dissociated and adsorption is relatively low, the polymer enhances dissolution of Ba. At pH 9, where adsorption is still significant (Fig. 1) and PAA is fully ionized,³⁶ there is a positive linear correlation between Ba dissolution and PAA concentration that does not appear to level off at high polymer concentrations. This is a clear indication that Ba is being sequestered by PAA in solution at basic pH values. This is the result of complex formation in solution but may involve adsorption of the polyelectrolyte as an initial step. Sequestering of Ca²⁺ via complex formation has been demonstrated for the aqueous apatite system in the presence of carboxyl-containing polymers.^{47–51} By complexing dissolved Ba²⁺, PAA effectively enhances solubility by acting as a Ba sink in solution. Above the pH_{iep} (approximately pH 10), the electrostatic interaction between PAA and the surface turns repulsive due to charge reversal, and at the same time, BaTiO₃ solubility decreases substantially (approximately 10⁻⁵ mol/l at pH 11). As a result of these two factors, only a small dissolution

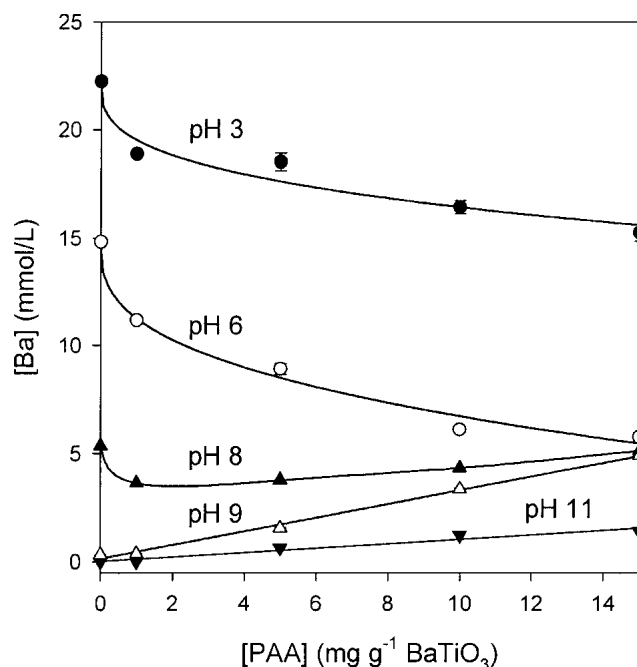


FIG. 5. Dissolved Ba as a function of PAA concentration (on a mass basis relative to BaTiO₃) and suspension pH. Error bars indicate standard uncertainty of replicate analyses.

enhancement is produced by PAA at pH 11, even at fairly high dosages; however, the dependence on polymer concentration is linear, as it is at pH 9.

At acidic pH values, where PAA adsorption is largely irreversible,³⁶ and the degree of ionization of PAA decreases significantly (approximately 40% of sites ionized at pH 6 and approximately 0% ionized at pH 3),³⁶ PAA exhibits passivating behavior that increases with increasing polymer concentration. Passivation (measured as a decrease in Ba concentration below that which is present in the absence of additives) increases with PAA dosage, with about 95% of the maximum effect being achieved at a concentration of about 1% (i.e., 10–12 mg of PAA/g of BaTiO₃) at both pH 3 and pH 6. Table I compares the total (adsorbed + free) concentration of PAA (normalized to unit surface area of the solid phase) in the system at 95% of Γ_{\max} with the total concentration at the point where roughly 95% of the maximum passivation effect has been achieved at each pH value. The close agreement between these values, in the neighborhood of 4 mg/m², suggests that the *adsorbed* polymer plays the principal role in passivating BaTiO₃. That is, after monolayer adsorption is reached, a further increase in PAA concentration has little effect on solubility, indicating that the excess free polymer is not involved in this process. In this case, surface-bound PAA either (i) forms a protective layer that kinetically inhibits further dissolution, (ii) complexes with surficial Ba²⁺ in a manner that stabilizes the surface layer and fixes the Ba, or (iii) acts simultaneously via both mechanisms.

Adsorption, electrokinetic, and solubility data, taken altogether, suggest that sequestering of Ba²⁺ from the BaTiO₃ surface is promoted by weak adsorption of anionic ligands onto fairly labile Ba²⁺ surface sites. When the adsorption interaction is strong (irreversible), as it is in acidic media, the polyelectrolyte forms a stable passivating layer. On the other hand, if adsorption is largely absent, due to unfavorable electrostatic interactions, then Ba²⁺ will be sequestered only as the ions are released into solution in accordance with the natural rate of BaTiO₃ dissolution. In other words, PAA is still capable of acting as a sink for Ba, but it is no longer actively involved in the process of removing Ba²⁺ from the substrate surface. In highly basic media, Ba²⁺ is strongly bound to the crystal lattice or surface, and the leaching rate is therefore very slow. Thus, at basic pH values above the pH_{iep} of the solid phase (approximately pH 10 in the present case), conditions are such that PAA is neither an effective sequestering agent nor a passivating agent.

The present results differ from both Lee²³ and Wang *et al.*,²⁸ who observed a passivating effect in the presence of polycarboxylates at basic pH values. In the former case, the pH of the experiment appears to have been around 10, while the pH_{iep} of BaTiO₃ used in that study was reported to be above pH 12. Therefore, conditions

of low solubility (i.e., nonlabile surficial Ba²⁺) and an attractive electrostatic potential between the fully ionized PAA and positive surface sites (leading to strong adsorption) should promote passivation according to our mechanistic arguments presented above. It is worth noting, however, that the experiments reported by Lee were performed at an elevated temperature (55 °C), well above that used in the present work, and only a single PAA dosage and pH were tested, limiting the comparative value of their results. The second study, Wang *et al.*, involved poly(aspartic acid), a polycarboxylate containing both amine and amide moieties. These authors found that Ba concentration in solution decreased at pH 12 with increasing polymer dosage, up to about 3 mg/g, which corresponds to an adsorbed amount of approximately 2 mg/g (near-saturation adsorption). This saturation level is roughly three orders of magnitude higher than what we observe for PAA at pH 9 in our system, and we anticipate near zero uptake for PAA at pH 12. The authors do not report the pH_{iep}, but zeta potential measurements indicate that it is below pH 10, meaning that the particles are negatively charged at the experimental pH. For PAA under these conditions, we would predict a neutral effect or possibly a very mild sequestering. The difference can be attributed to the additional basic moieties on poly(aspartic acid), which must play a significant role in the adsorption process, given the high adsorption isotherms reported at pH 12. Contrary to PAA, with a stronger, less reversible surface interaction (due to the presence of amine and amide moieties), a stable passivating layer is possible for poly(aspartic acid) under basic conditions.

The effect of PVA on the pH dependence of Ba dissolution is shown in Fig. 6. There is a marginal-to-moderate decrease in dissolved Ba in the presence of PVA at all experimental concentrations and pH values. However, the trend for pH values up to pH 8 indicates the maximum passivation effect at a relatively low dosage, followed by a gradual increase in dissolution at higher PVA concentrations (approaching the natural Ba solubility limit). It is clear that PVA does not sequester Ba²⁺ under the present experimental conditions. If PVA complexed strongly with Ba²⁺, we would expect to see either an enhanced solubility or a much larger passivation effect, depending on the reversibility and degree of adsorption. This confirms published studies that show PVA is only efficient at binding metal cations at or above pH 12.⁴² In the present work, at pH 9 and pH 11, Ba²⁺ concentration is reduced by 96% and 31%, respectively, at PVA dosages above 1 mg/g. Of course, the natural concentration of Ba²⁺ (without PVA or PAA) at these pH values is quite low to begin with (approximately 3.4 × 10⁻⁴ mol/l at pH 9 and approximately 1.6 × 10⁻⁵ mol/l at pH 11). In contrast, PAA caused an increase in solubility at these same pH values, with a linear dependence on polymer dosage.

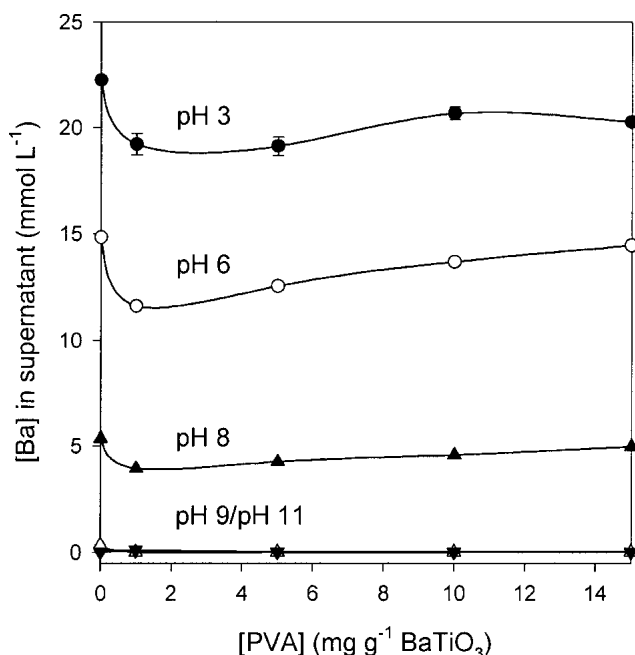


FIG. 6. Dissolved Ba as a function of PVA concentration (on a mass basis relative to BaTiO₃) and suspension pH. Error bars indicate standard uncertainty of replicate analyses.

It is notable at pH 8 that PAA and PVA provide almost identical passivating behavior in this system. For PVA, the behavior at pH 8, a mildly basic medium, is qualitatively similar to its behavior in acidic media. On the other hand, pH 8 appears to represent a transition state for PAA, which switches from a passivating agent below pH 8 to a sequestering agent above that value.

IV. CONCLUSIONS

The influence of ionizable PAA and nonionic PVA on the dissolution of Ba at the BaTiO₃-aqueous solution interface was investigated as a function of pH and polymer concentration. Both polymers exhibit passivating tendencies, although PAA exhibits both passivation and sequestration (enhancement of solubility) depending on the pH, whereas PVA provides marginal-to-moderate passivation throughout the entire experimental pH and PVA concentration range. Sequestering by PAA in basic solution above pH 8 is attributed to complexation of Ba²⁺ by anionic carboxylate groups and weak (reversible) adsorption. Under these conditions, dissolved Ba²⁺ exhibits a positive linear dependence on PAA concentration. A relatively strong passivation response is observed for PAA in acidic solution; the dissolved Ba²⁺ concentration decreases in a power-law behavior with increasing polymer dosage. This behavior indicates dissolution is inhibited either by the formation of a physical barrier, due to the dense adsorbed polymer layer, or because surface complexes between adsorbed carboxylate groups and

Ba²⁺ serve to stabilize the latter. These mechanisms likely act in unison, with surface complexes stabilizing the thick polymer layer.

With a consideration of past and present results, the basic characteristics of a good passivating agent for application to BaTiO₃ in aqueous media can be suggested. The agent should be of moderate chain length, long enough to facilitate multiple binding to the particle surface but without adversely increasing suspension viscosity or yield stress. The agent should contain anionic ligand groups capable of forming a weak complex with Ba²⁺ to help stabilize the metal cations on the particle surface without sequestering them. The agent might contain other hydrophilic or hydrophobic moieties that promote irreversible adsorption, even under conditions where electrostatic forces are repulsive for the anionic ligand sites. Finally, a partially coiled adsorption conformation should promote a denser, less permeable layer.

In terms of future work, a block copolymer, with one block containing nonionic water soluble moieties, and the other block containing anionic ligand groups, or a mixture of anionic and perhaps hydrophobic functionalities, may prove an efficient combination passivating/dispersing agent and would be worth exploring. Additionally, we are investigating the passivating behavior in mixed PAA/PVA polymer systems. On the basis of previously published studies,^{32,33} we expect that PAA will adsorb preferentially to, and/or displace, PVA in mixed systems (especially at acidic and moderately basic pH values) and thus should dominate the solubility behavior of BaTiO₃ in this case. On the other hand, in strongly basic media (pH > 10) the effect of a mixed system on dissolution of Ba²⁺ is less predictable due to weak adsorption by both PVA and PAA. The order of addition will also impact adsorption³² and will be examined in the context of Ba solubility.

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