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Influence of Dispersing Agents on the Solubility of Perovskites in Water

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In this study, solubility behavior of lead magnesium niobate (PMN) powders in water was investigated in the presence of pure polyacrylic acid and polyacrylic acid/polyethylene oxide comb polymers. Experiments were performed by measuring the solubility of PMN in terms of the concentration of Pb^{+2} and Mg^{+2} ions in supernatant as a function of pH and dispersing agent dosage. The concentrations of the metal ions in supernatant were found to be affected by the dispersant concentration, stirring time and the suspension pH. Results revealed that both dispersing agents enhance the cation dissolution from PMN surface at pH 9 due to weak (reversible) adsorption and complexation of Pb^{+2} and Mg^{+2} by carboxylate groups. On the other hand, under acidic conditions cation dissolution from PMN is inhibited and this was attributed to the strong adsorption of dispersing agents onto the powder surface and formation of a dense polymer layer.

Keywords Anionic polyelectrolyte, ceramics, comb like polymer, solubility, suspensions

1. INTRODUCTION

Lead magnesium niobate (PMN) is an important relaxor ferroelectric material with perovskite structure.[1–3] Because of the superior dielectric constant and electrostrictive coefficient it is employed in the manufacture of multilayer ceramic capacitors, actuators, transducers and electro-optic devices.[4,5] It also finds applications in motors, pumps, optical scanning systems, and vibration isolators.[6]

The manufacturing of multilayer electronic ceramic devices composed of perovskite materials such as PMN generally involves a colloidal process which requires preparation of stable suspensions.[7] Perovskite materials having the general chemical formula, ABO_3 such as PMN are composed of a cation at the A site that is generally soluble in water and a cation at the B site that is only slightly soluble over the most of the pH ranges.[8,9] Therefore, the leaching of lead magnesium niobate in water is a major issue in colloidal processing. The nonstoichiometry can be induced by leaching of Pb^{+2} and Mg^{+2} from PMN surface upon contact with water and this may cause some difficulties in controlling the final dielectric properties and the microstructure.[10] Especially deficiency of lead in PMN structure may cause formation of a undesired phase called pyrochlore which degrades the electrical properties.[11] Therefore, passivation at the PMN/water interface is essential for establishing reliable manufacturing of PMN based ceramic devices.

On the other hand, organic additives such as polyelectrolytes play a significant role in preparation of stable suspensions because they offer an effective means of modifying particle–particle interactions.[12] The polyacrylic acid (PAA) is a widely used polyelectrolyte in ceramic systems.[13–15] It contains ionizable carboxylic acid groups along its backbone. These groups dissociate and form negatively charged carboxylate groups at high pH. Similarly, polyacrylic acid/polyethylene oxide (PAA/PEO) comb polymers can be employed as novel dispersants in ceramic systems. They are very effective stabilizing agents especially for aqueous multi-component metal oxide suspensions such as barium titanate and cement.[16,17] The previous study of Şakar-Deliormanlı et al. showed that PAA/PEO comb polymers are also effective dispersants for PMN/water system.[18] PAA/PEO comb polymers impart stability to PMN suspensions over a wide pH range and ionic strength where pure PAA fails. The presence of PEO teeth shields the PAA backbone from ion interactions.[16]

It is known that polymers containing carboxylic acid groups form ionic bonds with the metal surface and this

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reduces the polymer desorption.[19] Kislenko and Verlinskaya showed that polymers containing active functional groups such as PAA can be adsorbed on the zinc oxide, interact with them to form complexes then desorp and thereby increase the zinc ion concentration in solution.[19] Similarly, the effect of anionic dispersing agents on the solubility of kaolin was studied by Zaman and Mathur.[20] They proved that concentration of the aluminum and silicon ions in kaolin suspensions is highly affected by the dosage of the dispersing agents and the slurry pH. Paik and co-workers investigated the effect of polyacrylic acid and polyvinyl alcohol on the solubility of colloidal $BaTiO_3$ in an aqueous medium. They showed that both polymers exhibit passivating tendencies but PAA exhibits both passivation and sequestration (enhancement of solubility) depending on the pH.[10]

Solubility characteristics of bare PMN powders in aqueous medium has been studied studied in the past.[21] Similarly, effect of PAA and PAA/PEO on the dispersion/flocculation behaviour of aqueous PMN suspensions and their adsorption mechanism onto PMN surface have been well investigated.[18,22] However effect of these dispersing agents on the solubility of PMN was not reported yet. Therefore, the goal of this study was to investigate the influence of PAA and PAA/PEO comb polymers on the stability of PMN/water interface. In the study Pb^{+2} and Mg^{+2} ion leaching from PMN surface was analyzed as a function of dispersing agent concentration, stirring time and suspension pH.

2. EXPERIMENTAL

2.1. Materials

Lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$ powder which was produced by combustion spray pyrolysis method provided by Praxair Specialty Ceramics (Woodinville, WA, USA). Powder purity is 99.9% as reported by the manufacturer. Bulk density (Helium pycnometer Micromeritics 1330, Norcross, GA, USA), and the BET surface area (Model ASAP 2400, Micromeritics, Norcross, GA, USA) of the powder are measured to be $7.967\,g/cm^3$ and $1.168\,m^2/g$, respectively. Particle size distribution of the powder was obtained using a particle size analyzer (Model CAPA-700, Horiba, Ltd, Tokyo, Japan) and the d_{50} of the powder was measured to be $2.03\,\mu m$.

Polyacrylic acid graft polyethylene oxide comb polymers PAA/PEO (M_w: 25800 g/mol, W.R. Grace and Co. Connecticut, Cambridge, MA) pure PAA (M_w: 5000 g/mol, Polyscience Inc., Warrington, PA) were employed as the dispersant for the aqueous PMN suspensions. The comb polymer consists an anionic PAA backbone (M_w: 5000 g/mol) with ionizable carboxylic acid group (COO^-) per monomer unit and charge neutral PEO teeth (M_w:2000 g/mol) grafted onto the backbone at random intervals through ester linkages (acid:ester ratio 7:1). Figure 1 shows the chemical structure of the PAA and PAA/PEO comb polymer used in this study.

2.2. Method

2.2.1. *Solution Preparation*

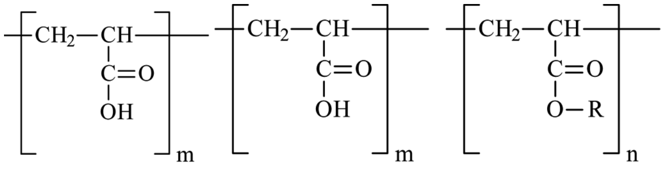
Dilute polymer solutions were prepared by adding an appropriate amount of polymer to deionized water. The pH was adjusted using either a 0.1 M solutions of HNO_3 or NH_3OH. The polymer solutions were magnetically stirred for 0.5 hours to allow for equilibration. 1 M solutions of KNO_3, $MgCl_2$, $LaCl_3$ were prepared by dissolving KNO_3, $MgCl_2 \cdot 6H_2O$ (Fisher Chemicals, Fair Lawn, NJ, USA) and $LaCl_3$ (Fisher Chemicals) in deionized water. These salt solutions were used to vary the monovalent, divalent, or trivalent salt concentration of the polymer solutions. To investigate the complexation behavior of Pb^{+2} with polyelectrolytes, lead(II) acetate trihydrate, $(Pb(CH_3COO)_2.3H_2O$, 99.5%, Riedel-de Haen) was used. After adjusting the ionic strength, solutions were magnetically stirred for another 0.5 hours for equilibration.

2.2.2. *Suspension Preparation*

Lead magnesium niobate suspensions were prepared at 10 vol% in the absence and presence of PAA/PEO comb polymers and PAA. After PMN powder was added to the stock solution of polymeric dispersant, the suspension was ultrasonicated for 2.30 minutes using a 1s on/off pulse sequence. The suspension pH was adjusted using HNO_3 and NH_4OH solutions. Suspensions were magnetically stirred for 24 hours at room temperature prior to measurements.

2.2.3. *Dynamic Light Scattering*

Dynamic light scattering (DLS) measurements (Zetasizer 3000HS, Malvern Instruments Ltd., UK) were carried out on dilute polymer solutions, (5 mg/ml and pH 9) of varying salt concentration to determine their hydrodynamic radius (R_H) as a function of counterion concentration. A refractive index, n, of 1.53, and 1.47 was used during the measurements for PAA and PAA/PEO,



(a) (b)

FIG. 1. Chemical structure of (a) PAA and (b) PAA/PEO comb polymers $R = (CH_2CH_2O)_x\text{-}CH_3$, $x = 45$.[26]

respectively. The DLS unit utilizes a He-Ne laser at a wavelength of 632.8 nm with a laser power of 10 mW. The scattered light was collected at an angle of 90°. A virgin polystyrene cuvette was used for each measurement.

2.2.4. Turbidity Measurements

Dilute polymer solutions (5 mg/ml) were prepared by adding an appropriate amount of PAA or PAA/PEO comb polymer to deionized water. The turbidity of dilute polymer solutions of varying pH and salt concentration was measured by a turbidimeter (WTW 555, Germany). Turbidity is an optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample. The turbidimeter used in this study measure the light scattered at an angle to the incident light beam and then relate this angle scattered light to the samples turbidity.[23] Measurements were performed using nephelometric ratio method and results were recorded in terms of NTU with ±2 of value or ±0.01 NTU accuracy.

2.2.5. Cation Dissolution

Solubility of Pb^{+2}, Mg^{+2}, and Nb^{+5} ions in the PMN structure was examined using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES Optima 2000 DV Perkin Elmer Norwalk, CT, USA). For this purpose, suspensions prepared at 10 vol% according to the procedure described in the previous section were centrifuged at 4000 rpm for 1 hour to obtain a clear supernatant. Supernatants were further filtered from 0.02 µm microfilters to eliminate any possible particles in solution. The amounts of Pb^{+2}, Mg^{+2}, and Nb^{+5} in particle-free supernatants were determined using ICP-AES at different pH values and as a function of dispersant concentration.

3. RESULTS AND DISCUSSION

3.1. Hydrodynamic Radius of the Polymers

Figure 2 shows the hydrodynamic radius (R_H) of the PAA/PEO comb polymer and PAA as a function of monovalent and divalent salt additions. The hydrodynamic radius which includes both solvent (hydro) and shape (dynamic) effects provides a measure of the size of the polyelectrolytes in solution.[24] To make comparison between the salt species of having different valency the graph is plotted (R_H) versus [I]/[COO^-] where [I] is the ionic strength and [COO^-] is the molar concentration of ionized carboxylic acid groups.[16]

As it is shown in Figure 2, the hydrodynamic radius values are measured to be 4.9 and 8.0 nm for PAA and PAA/PEO, respectively under fully ionized conditions at pH 9. Results agree with the previous study of Kirby et al.[16] Results also suggest that PAA solution stability changes dramatically as the ionic strength increases. The hydrodynamic radius of PAA reduces to ~2 nm at high ionic strength conditions. Additionally, both monovalent and divalent salt species do some effect on the transition of PAA to coiled structure. An important characteristic of PAA is its ability to undergo expansion from a coiled to a stretched conformation by the increase in charge density the chain. This transition is due to electrostatic repulsion between neighboring ionized sites. Dissociation of each carboxyl group along the polymer chain significantly affects the ionization of neighboring groups. As a consequence of electrostatic interactions, dissociation becomes difficult as the fraction of ionized sites increases. The effect is analogous to the well-known helix–coil transition that is associated with polypeptides.[14,25]

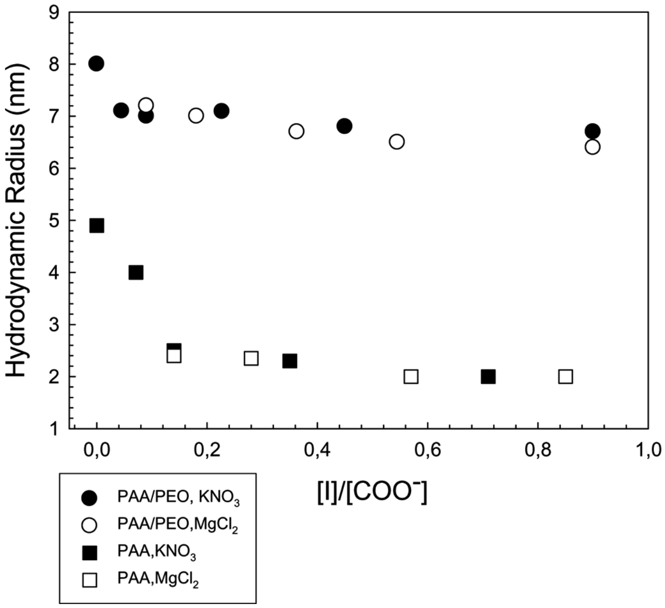


FIG. 2. The hydrodynamic radius of PAA and PAA/PEO solutions as a function of monovalent and divalent salt additions. Where $[I]=\frac{1}{2}\sum n_i z_i^2$ due to added salt only, $[COO^-]=0.07$ for PAA, and 0.011 for PAA/PEO.

On the other hand, results revealed that stability of PAA/PEO comb polymers is not affected by the salt concentration. Even in the presence of divalent salt species a decrease in the R_H was not observed. The different response to ionic strength modification in two polyelectrolytes were attributed to the presence of the PEO teeth in the comb polymer which prevents large conformational changes in ionized conditions.

3.2. Turbidity Measurements

Turbidity measurements were carried out on dilute polymer solutions of varying pH and salt concentration. Figures 3 to 6 show the turbidity values of polymer solutions as a function of ionic strength and pH. The stable polymer solutions characterized in which the polymeric

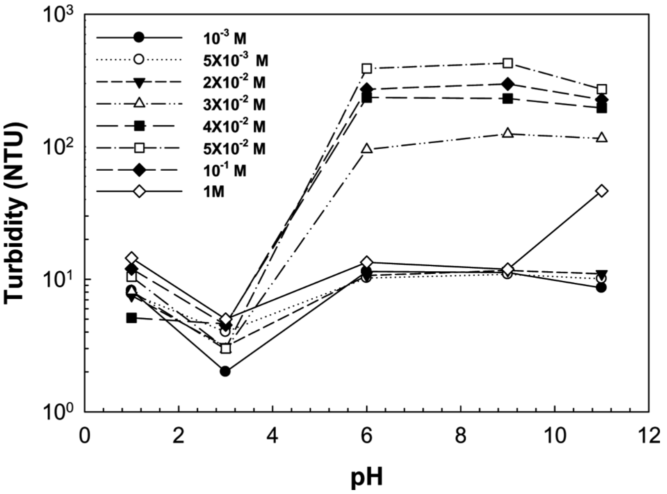


FIG. 3. Effect of $MgCl_2$ concentrations on the turbidity of PAA solutions as a function of pH.

species remain well solvated and are transparent. Therefore, high turbidity values correspond to the solutions having low stability.

As it is shown in Figure 3 in the presence of divalent salt additions ($MgCl_2$) the stability of PAA solutions depends on the divalent salt concentration. Under fully ionized conditions (pH 9) PAA solutions were only stable in the range $0–2 \times 10^{-2}$ M $MgCl_2$. At higher salt concentrations PAA start to make complexes with Mg^{+2} ions in solution and turbidity increases.

Effect of trivalent cations on the stability of PAA and PAA/PEO comb polymer is shown in Figures 4 and 5. Kirby reported that dilute polymer solutions with trivalent, $LaCl_3$ additions could not be prepared above pH 7 due to the precipitation of lanthanum hydroxide that would alter the turbidity results.[26] However, this pH value is only slightly below the pH required for full ionization of the PAA-based species (pH 9). Accordingly, the results of the current work showed that at pH 3 presence of $LaCl_3$ did

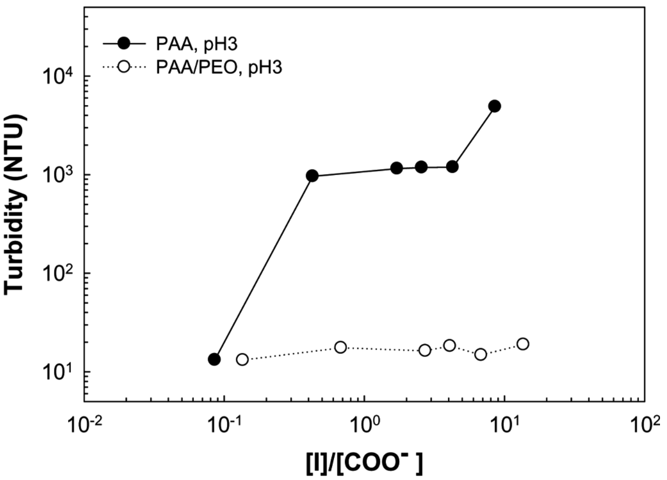


FIG. 4. Effect of $LaCl_3$ on the turbidity of PAA and PAA/PEO solutions at pH 3.

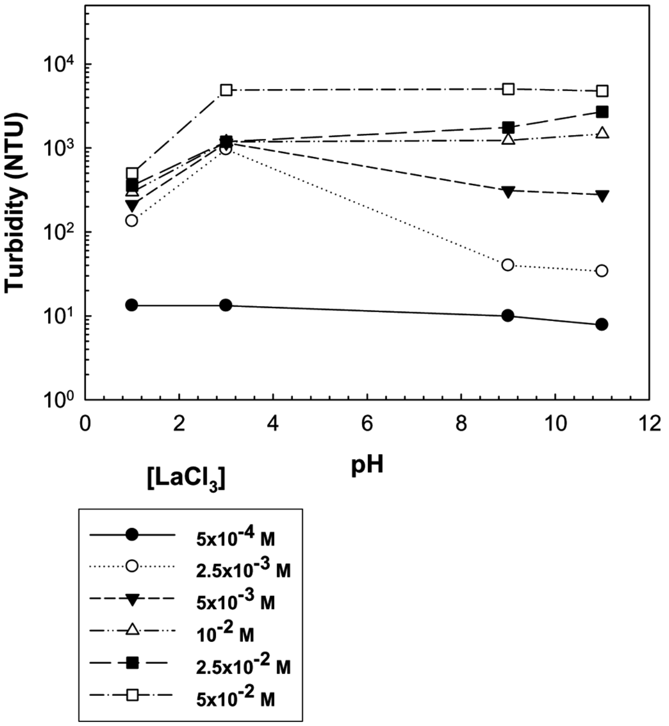


FIG. 5. Effect of $LaCl_3$ concentration on the turbidity of PAA solutions as a function of pH.

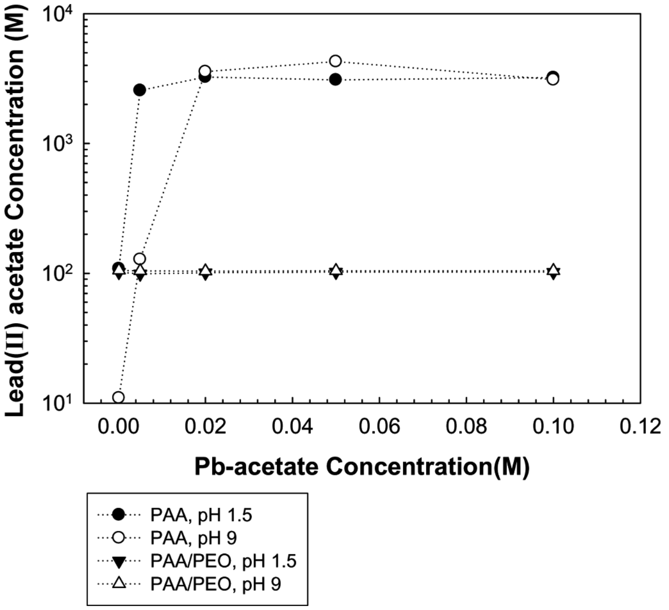


FIG. 6. Effect of lead(II) acetate concentration on the turbidity of PAA and PAA/PEO solutions at pH 1.5 and pH 9.

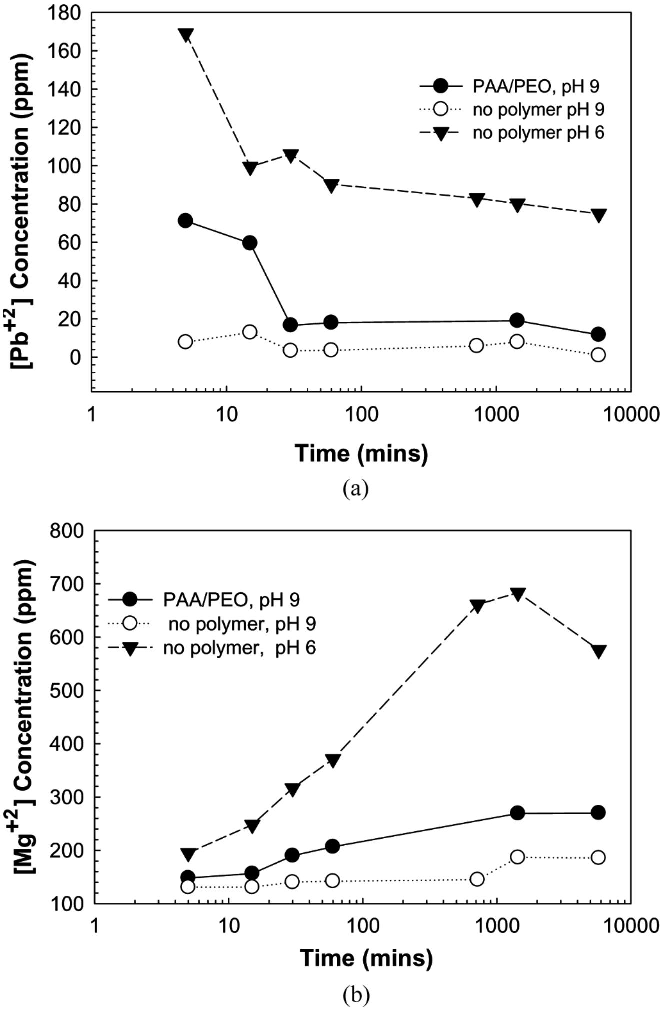
not affect the stability of comb polymer solutions. However, a sharp increase was observed in the turbidity of PAA solutions due to PAA-La^{+3} complexation (see Figure 4). The complex formation initiate at 2.5×10^{-3} M $LaCl_3$ but the maximum turbidity value was obtained at 5×10^{-2} M $LaCl_3$. On the other hand, the increase in turbidity of the PAA/PEO comb polymer solutions at pH 9 in the presence of $LaCl_3$ may be attributed to the precipitation of ions and formation of $La(OH)_3$.

To investigate the interaction of PAA and PAA/PEO comb polymers with the Pb^{+2} ions in solution, turbidity measurements were performed in the presence of lead(II) acetate. First of all, turbidity of pure lead acetate in water was investigated. It is known that Pb(II)acetate with water forms $Pb(CH_3COO)_2 \cdot 3H_2O$ which is a colorless crystalline substance. Turbidity of Pb(II) acetate solution at 5×10^{-2} M started to increase at pH 6 and persist to increase as the pH increases. Figure 6 show the effect of Pb^{+2} ion addition on the stability PAA and comb polymer suspensions. Under very acidic and basic conditions no interaction between comb polymer and Pb^{+2} was observed. On the other hand, even at pH < 6 an increase was noticed in the turbidity of PAA solutions in the presence of small amount of lead(II) acetate.

3.3. Cation Dissolution from PMN in the Presence of Dispersing Agents

It is known that, PMN incongruently leach Pb^{+2} and Mg^{+2} ions at the interface below pH 10 and therefore the ionic concentration in suspension increases.[21] Especially the Pb^{+2} concentration increases dramatically in the acidic region. Though the Mg^{+2} dissolution is also pH dependent the dissolution rate is almost an order of magnitude smaller compared to that observed with Pb^{+2} at low pH values. On the other hand, Nb^{+5} exhibites rather low dissolution under the same conditions. Dissolution mechanism of cations from PMN surface can be explained as follows: In the first step Pb^{+2} and Mg^{+2} must diffuse out through a growing reactive surface layer. In the final stage, dissolution slows considerably and following possibilities may arise: a steady-state equilibrium concentration is reached, a thick the depletion layer may form and leads to passivation; or the particles are completely converted to Nb-rich phase.[21,27]

In the current study, the Pb^{+2} and Mg^{+2} ion leaching from PMN surface was studied in the presence of PAA and PAA/PEO comb polymers as a function of polyelectrolyte concentration. Experiments were performed for a solids loading of 10 vol% at different pH and ionic strength conditions. Figure 7 displays the Pb^{+2} and Mg^{+2} ion concentrations of PMN suspensions in the presence of PAA/PEO as a function of string time. Results show that Pb^{+2} and Mg^{+2} concentration reaches a considerable level immediately after the powder addition and then Pb^{+2} concentration decreases and Mg^{+2} concentration increases with time. In the presence of comb polymer Pb^{+2} concentration in suspension was nearly 10 times higher compared to lead concentration of suspensions in absence of dispersant. Neubrand and co-workers observed similar behavior for Ba^{+2} dissolution from barium titanate surface as a function time.[28]



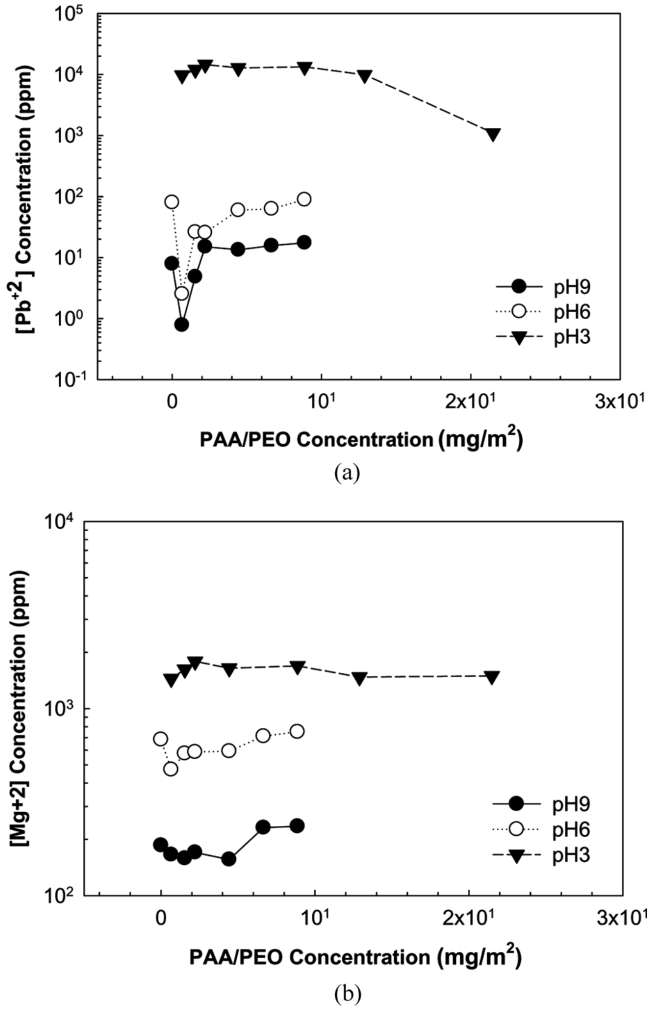
(a)

(b)

FIG. 7. Effect of PAA/PEO (10 mg/ml) on the leaching of (a) Pb^{+2} and (b) Mg^{+2} in PMN suspension (10 vol%) as a function of stirring time.

It is possible to explain the decrease in lead concentration by re-adsorption of Pb^{+2} ions to the hydrated PMN surface. Surface charge of the PMN is negative at pH 10.[21] Because of the negative surface charge Pb^{+2} ions may be re-adsorbed onto the surface and this may cause a decrease in Pb^{+2} concentrations in solution. Another explanation for the decrease observed in lead amount may due to the complex formation such as PbOH or $Pb_4(OH)_4^4$.[29]

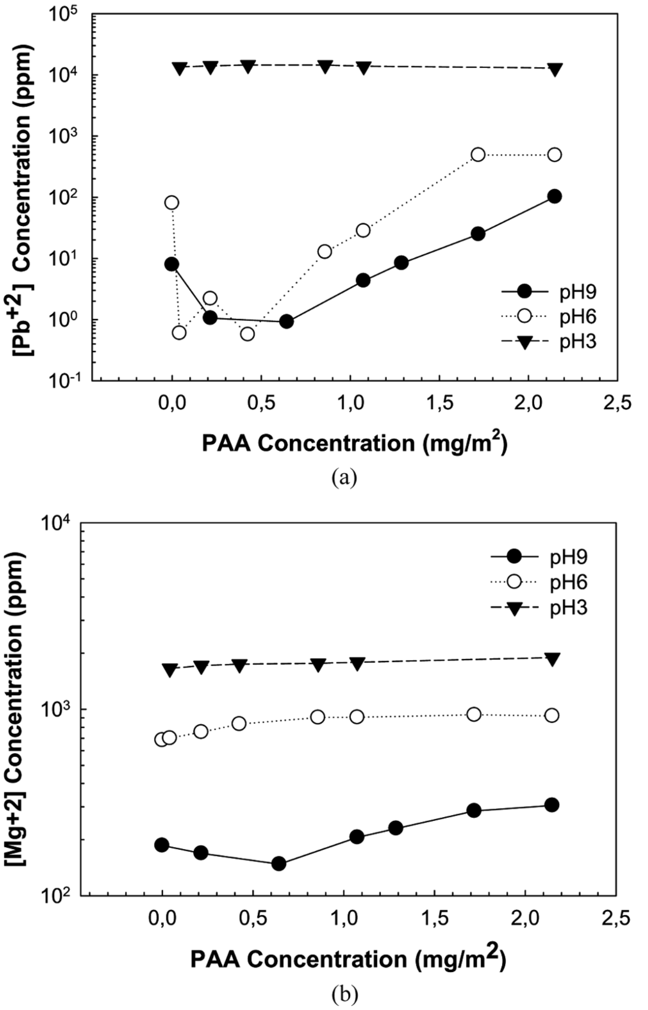
Figures 8 and 9 demonstrate the effect of PAA/PEO comb polymers and PAA on the solubility of PMN as a



(a)

(b)

FIG. 8. Effect of PAA/PEO concentration on the leaching of (a) Pb^{+2} (b) Mg^{+2} in PMN suspension (10 vol%) at pH 9, 6, and 3.



(a)

(b)

FIG. 9. Effect of PAA concentration on the leaching of (a) Pb^{+2} (b) Mg^{+2} in PMN suspension (10 vol%) at pH 9, 6, and 3.

function of polymer concentration and suspension pH, respectively. Both polyelectrolytes enhanced the solubility of PMN and caused an increase in the Pb^{+2} and Mg^{+2} ion concentration in solution at pH 6 and pH 9. Furthermore, an increase was observed in Pb^{+2} and Mg^{+2} concentrations in solution as the polyelectrolyte concentration increase.

Paik and coworkers investigated the effect of PAA on the solubility of barium titanate in aqueous medium. Results showed that Ba^{+2} sequestered by PAA in solution at basic pH values. At pH 8 and higher where PAA is well dissociated and the adsorption is low and the polymer enhanced the dissolution of Ba^{+2}. They attributed this result to the complex formation in solution but it may also involve adsorption of PAA as an initial step.[10] On the other hand, at acidic pH values where PAA adsorption is largely irreversible PAA causes passivation and this effect increases polymer concentration. Therefore, when the adsorption interaction is strong it is irreversible the polyelectrolytes form a stable passivating layer. In this case surface bound PAA either forms a protecting layer that inhibits the dissolution or complexes with cations in a manner that stabilizes the surface layer and fixes the cations. On the other hand, if adsorption is largely absent due to unfavorable electrostatic interactions then cations will be sequestered only as the ions are released into the solution in accordance with the natural rate of the oxide dissolution.[10]

Previously we have investigated the adsorption behavior of PAA and PAA/PEO onto PMN surface.[22] Results indicated that adsorption increases with decreasing pH for both PAA and PAA/PEO solutions. The adsorption isotherms for PAA at pH 3 was described as high affinity type and characterized by a strong adsorption. In contrast, at pH 9 isotherms correspond to nonhigh affinity type with most of the polymer remaining free in solution. Similarly, PAA/PEO comb polymer showed a low affinity adsorption nearly at all pH values. Results also revealed that for both of the polyelectrolytes under investigation the adsorption amount was slightly higher in the presence of $MgCl_2$. It has shown that in the presence of PAA, addition of $MgCl_2$ increased the adsorption nearly 2.6 times. It is possible to attribute this increase to the complex formation between PAA and Mg^{+2} ions. On the other hand, the increase in the adsorption of PAA/PEO onto PMN in the presence of monovalent or divalent salt was attributed to the decrease in the electrostatic forces rather than complex formation with the divalent metal ions in solution.[22]

Similarly, Vermohlen et al. investigated the effect of Ca^{+2} on the adsorption of acrylic based polyelectrolytes onto oxide surfaces. It was found that the adsorption is greatly increased by Ca^{+2} ions.[30] This is because multivalent cations can bind to the carboxyl functional groups of the polyelectrolyte to form PAA-cation complexes (R-COO—M^{+2}—OOC-R) in solution. This complexation can promote the adsorption by lowering the net charge of the polyelectrolyte or by decreasing the solubility of the complex in solution.[31]

Our previous studies showed that cation concentration in PMN suspensions (10 vol%) at pH 3 was about 25000 ppm.[21,29] However, results obtained in the current study revealed that Pb^{+2} concentration is around 12500 ppm in PMN suspensions in the presence of comb polymer under the same conditions. Similarly, Pb^{+2} concentration is measured to be 13000 ppm in supernatant in the presence of PAA. Therefore, it is possible to conclude that in the presence of polyelectrolytes under acidic conditions cation dissolution from PMN surface is inhibited due to strong adsorption. This behavior also indicates that dissolution is inhibited by the formation of a physical barrier due to the dense adsorbed polymer layer.[10]

In the current study, sequestering of Pb^{+2} and Mg^{+2} from the PMN surface may be attributed to the weak reversible adsorption of anionic PAA and PAA/PEO comb polymer onto fairly unstable Pb^{+2} and Mg^{+2} surface sites at high pH values. Furthermore, by complexing dissolved cations, PAA enhances the solubility by acting as a Pb^{+2} and Mg^{+2} sink in solution.

4. CONCLUSIONS

Effect of PAA and PAA/PEO comb polymers on the solubility of PMN in water was investigated in this paper. Results revealed that both dispersing agents enhances the cation dissolution from PMN surface at pH 9. Sequestering of Pb^{+2} and Mg^{+2} from the PMN surface may be attributed to the weak adsorption of anionic PAA and PAA/PEO comb polymer onto fairly unstable Pb^{+2} and Mg^{+2} surface sites. On the other hand, a decrease in solubility was observed at pH 3. It was concluded that in the presence of polyelectrolytes under acidic conditions cation dissolution from PMN surface is inhibited due to strong adsorption. Results showed that the cation release from PMN surface is also dependent on the polymer concentration in suspensions.

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