

Potentiometric Titration of Poly(acrylic acid)s with Various Mean Molecular Weights in the Presence of Calcium Ion

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*Key words: Poly(acrylic acid), Molecular weight, Potentiometric titration,
Calcium ion, Polycarboxylate cement*

Abstract

The binding of free calcium ions in aqueous solutions of poly(acrylic acid)s (PAAs) with various mean molecular weights (MMWs) were studied by potentiometric titration of their PAAs and a free calcium ion in the solution was measured by the calcium ion electrode. The binding molar ratio between the carboxy group and Ca^{2+} was about 2 : 1 for the PAAs (35×10^4 MMW, 4×10^{-3} M), and about 3 : 1 for the concentration of 8×10^{-3} M. The reaction of the PAAs with Ca^{2+} was affected by the molecular weight and concentration of the PAAs. For example, the precipitation reaction occurred, when the concentration of the PAAs with 100×10^4 MMW was 4×10^{-3} M and the concentration of Ca^{2+} in the solution was 8 mM and when that of the PAA with 35×10^4 MMW was 8×10^{-3} M and Ca^{2+} was 16 mM. Their precipitates contained the unreacted carboxy groups with calcium. The molecular weight and concentration of PAA and the unreacted carboxy groups affected the tensile bond strength of the polycarboxylate cements using poly(acrylic acid), e.g., the bond strength to stainless steel became maximum at about 15×10^4 MMW.

Introduction

The polycarboxylate cement has a high adhesive ability to the tooth substrate and dental alloys. Therefore, the cement is extensively used in clinical dentistry. The adhesive mechanisms of the cement to tooth substrate is considered to be due to the chemical bond of the carboxy groups in the cement polymer with the inorganic tooth substrate^{1,2,3)}. However, the mechanism has not been clearly elucidated. For example, 1. Reactivity of calcium with the carboxy groups due to the differences of the mean molecular weight (MMW) and concentration of poly (acrylic acid) (PAA) in the cement liquid. 2. Relationship between the bond strength of the cement and the MMW of PAA. 3. Aggregation state between the calcium in the tooth

substrate and the cement powder and the carboxyl group in the hardened cement. In this study, to investigate the binding of free calcium ions and the carboxy groups in aqueous solution using PAAs with various MMW, potentiometric titration of their polyelectrolytes was carried out, and a calcium ion electrode was used to measure the free calcium ion in the solution.

Materials and methods

1. Preparation of PAAs and titrants

PAAs : Acrylic acid monomer, ammonium persulfate as initiator, distilled water (DW), isopropyl alcohol (IP) as chain transfer and hydroquinone (HQ) as inhibitor were placed into glass tube, the tube was sealed, and then was heated in a water bath at 55°C for 20 hours.

The PAAs with various MMWs were obtained under the condition of varying amount of DW, IP and HQ and at heating temperature of 60 to 90°C.

The reactant was diluted with distilled water and dialyzed with Spectra/por membrane (mwco:1000, SPECTRUM MEDICAL INDUSTRIES INC.) to remove a residual monomer. The water in the dialyzed solution was evaporated under reduced pressure with an aspirator and then the concentrated solution was lyophilized. The PAAs with various MMWs were obtained. The MMW of the PAAs were estimated by HPLC.

Titrant: About 0.18g of PAAs with various MMWs were dissolved in distilled water and made up to 500 ml. The factor was calculated from potentiometric titration curve of the PAA solution with 0.05 mol/l (mol/l was abbreviated as M) NaOH (factor:1.154) in the presence of 0.2 mmol of calcium ion. The concentration of the PAAs was about 5×10^{-3} M as carboxy group.

0.05 M Ca^{2+} solution : Calcium nitrate (ca. 5.9 g) was made up to 500 ml with distilled water. The factor was calculated from the end-point based on the titration of the calcium solution with a standard solution of EDTA and the value was 1.000. The same system containing Al^{3+} ion instead of Ca^{2+} ion was titrated. **0.05 M Al^{3+} solution :** $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Ca. 1.8 g) was made up to 100 ml with distilled water and pH of the solution was 3.02. Prior to the titration, 1.33 ml or 2.00 ml of the Al^{3+} solution was pipetted in a beaker, controlled pH of the solution to about 6.5 with 0.6 M and 0.05 M of NaOH, and then adjusted to 10 ml with distilled water. The mixture of 10 ml of the solution and 40 ml of 5×10^{-3} M PAA solution was titrated with 0.05 M NaOH.

2. Potentiometric titration

Some definite volume of 0.05 M $\text{Ca}(\text{NO}_3)_2$, 4 ml, and 40 ml of 5×10^{-3} M PAA solution were added in 100 ml beaker and the solution was made up to 50 ml with distilled water, and furthermore 1

ml of ion strength adjustment solution (4 M KCl) was added. The concentration of the carboxy group in 51 ml of the solution was about 3.98 mM. Calcium and hydrogen electrode were set in the solution, and the solution was titrated with 0.05 M NaOH in the presence of different concentration of $\text{Ca}(\text{NO}_3)_2$ under nitrogen atmosphere⁴⁾. The changes in pH and Ca^{2+} with titration were measured with a pH meter (D-12, HORIBA Co.) and Ca^{2+} ion analyzer (901, ORION Co.).

Results

1. Potentiometric titration curves of PAAs

Potentiometric titration curves of the PAAs with various MMWs without Ca^{2+} were shown in Fig.1. The pH curves of the PAAs were higher than that of isobutyric acid and were not dependent on the differences of the MMWs of the PAAs. The pH curves of the PAAs in the presence of Ca^{2+} were shown in Fig.2. All curves of the PAAs with up to 40×10^4 MMW were similar and were not dependent on the content of Ca^{2+} and the MMW of the PAAs. However, the curve of the PAA with 100×10^4

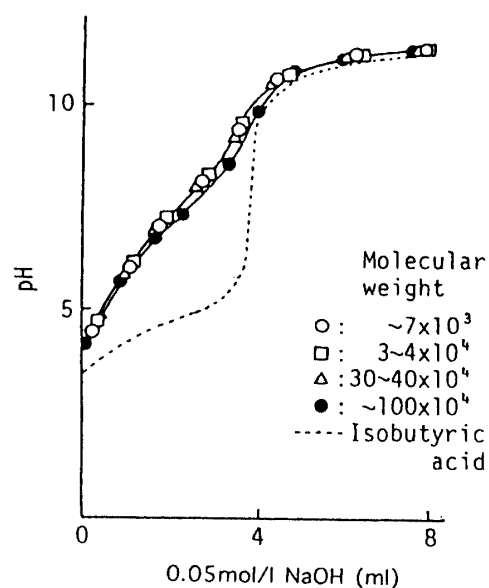
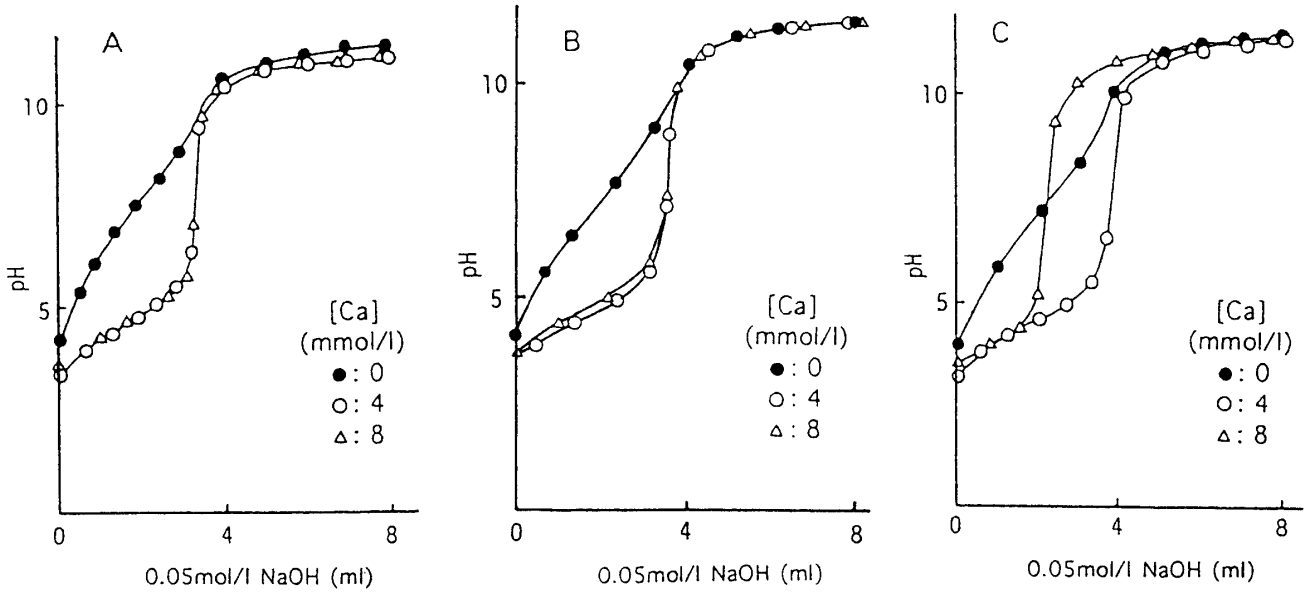


Fig.1 Potentiometric titration curves of PAAs (4×10^{-3} M, 50 ml) with NaOH together with one of isobutyric acid for comparison.



Mean molecular weight; A: $3 \sim 4 \times 10^4$, B: $30 \sim 40 \times 10^4$, C: $\sim 100 \times 10^4$

Fig.2 Potentiometric titration curves of PAAs (4×10^{-3} M, 50 ml) containing various concentrations of calcium ions with NaOH.

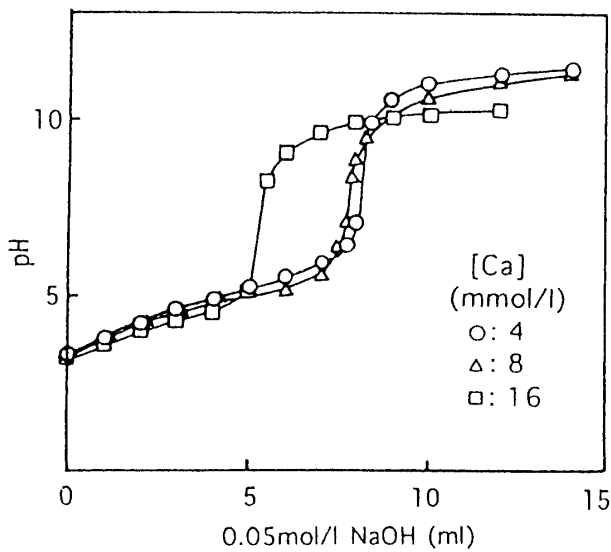


Fig.3 Potentiometric titration curves of PAA (4×10^{-3} M, 50 ml) containing various concentrations of aluminum ions with NaOH.

MMW was affected by the content of Ca^{2+} . In the content of 8 mmol of Ca^{2+} , the curve of the PAA moved toward the low volume of the NaOH. The titration curves of the PAA with 35×10^4 MMW (8×10^{-3} M) were shown in Fig.3. The concentration of the PAA was twice that of the PAA in Fig.2. The end-point of the curve

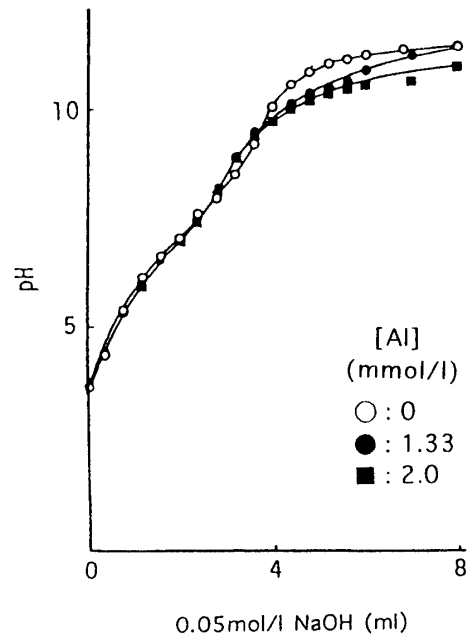


Fig.4 Potentiometric titration curves of PAA (MMW: 35×10^4 , 8×10^{-3} M, 50 ml) containing various concentrations of calcium ions with NaOH.

moved to a low value of NaOH when the concentration of Ca^{2+} was 16 mM. On the other hand, the pattern of the titration curves of the PAA solution containing Al^{3+} were same that of

the PAA solution without Al^{3+} (Fig.4).

2. Binding ratio of the carboxy groups and Ca^{2+}

The titration curve of the PAA (35×10^4 MMW) with NaOH in the presence of 3.92 mM Ca^{2+} , equal to the concentration of the carboxy groups,

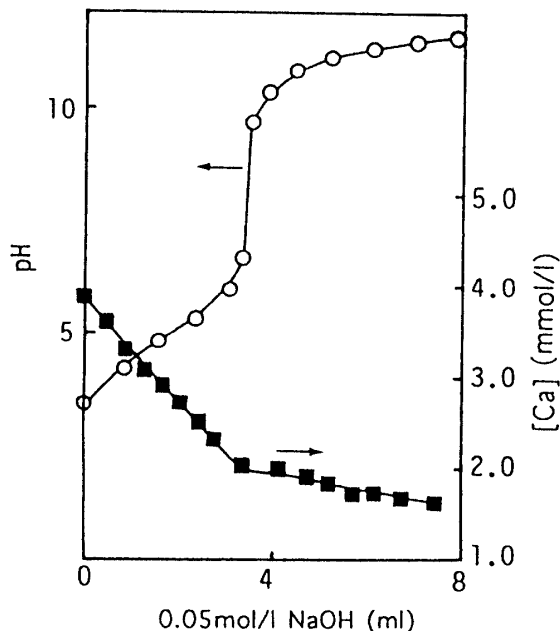


Fig.5 Potentiometric titration curves of PAA (MMW: 35×10^4 , 4×10^{-3} M, 50 ml) with NaOH and the concentration of free calcium ions in the solution.

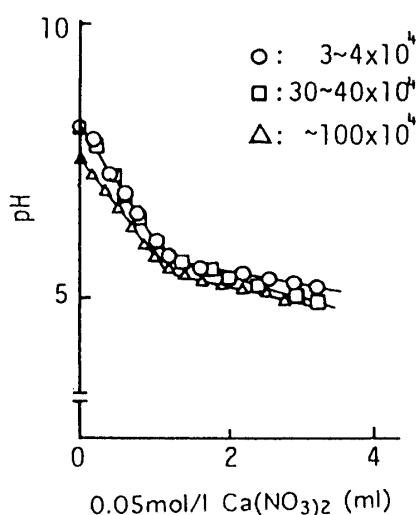


Fig.6 Potentiometric titration curves of the mixtures of PAAs with various MMWs (3.5×10^4 , 35×10^4 , 100×10^4 , 5×10^{-3} M, 40 ml) and NaOH (0.05 mol/l, 2 ml) in 50 ml with $\text{Ca}(\text{NO}_3)_2$.

was shown in Fig.5. The concentration of free Ca^{2+} in the solution linearly decreased and the line bent at the end-point. The moderate decrease of the concentration of Ca^{2+} from end-point is due to the increase of the volume of NaOH added. Therefore, the initial decrease up to the end-point corresponds to the decreased amount of Ca^{2+} bonded to PAA in the solution. The corresponding concentration of Ca^{2+} was 1.92×10^{-3} M and was half of that of the carboxy groups in the PAA solution. It was found that the binding molar ratio of the carboxy group and Ca^{2+} was about 2 : 1. A mixture of the PAA (5mM, 40 ml (0.2 mmol)), NaOH (0.05 M, 2 ml 0.1 mmol) and 8 ml of H_2O was titrated with 0.05 M $\text{Ca}(\text{NO}_3)_2$ and the pH curve of was shown in Fig.6. The amount of NaOH added was 0.1 mmol and was half that of the carboxy groups in the PAA solution. The carboxy anions produced by neutralization of the PAA with NaOH was 0.1 mmol and react with Ca^{2+} in the solution. The bending-point of pH in Fig.6 shows that all of the produced carboxy anion bonded to Ca^{2+} . The amount of the bonded Ca^{2+} was about 0.05 mmol that was calculated from the volume of $\text{Ca}(\text{NO}_3)_2$ at the bending-point, and was half the carboxy anion.

3. Precipitation reaction of PAA and Ca^{2+}

The precipitation reaction occurred, when the concentration of the PAA with 100×10^4 MMW was 4×10^{-3} M and the concentration of Ca^{2+} in the solution was 8 mM and when that of the PAA with 35×10^4 MMW was 8×10^{-3} M and Ca^{2+} was 16 mM. Production range of the PAA/ Ca precipitates on the concentration of Ca^{2+} and OH^- is shown in Fig.7.

4. Tensile bond strengths of the cements using the PAAs

Tensile bond strengths of the cement using the PAAs with various MMWs to stainless steel were shown in Fig.8¹⁰. The bond strength became maximum at a MMW of about 15×10^4 .

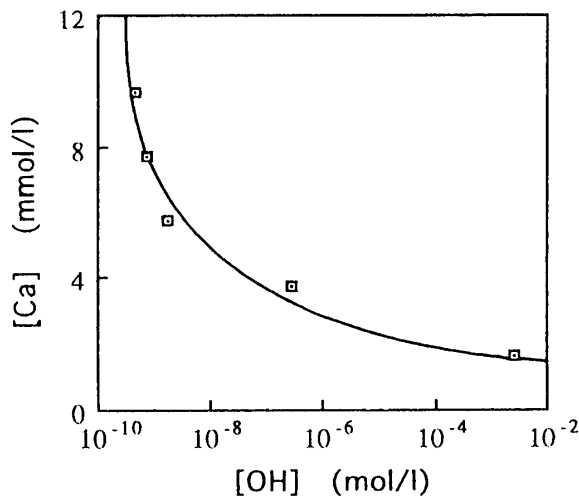


Fig.7 Precipitating ranges of PAA/Ca products for the concentrations of Ca^{2+} and OH^- .

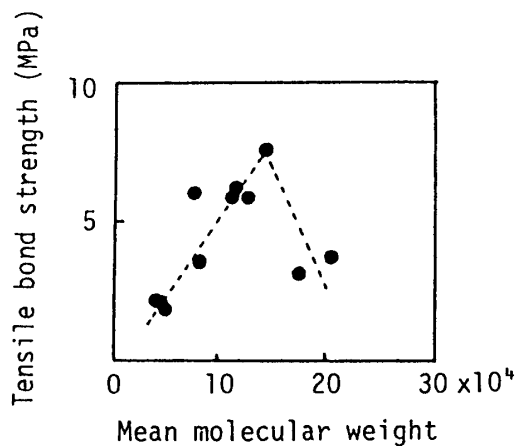


Fig.8 Effect of mean molecular weight of the PAAs on tensile bond strength.

Discussion

1. Potentiometric titration curves of PAAs

It is already reported that the carboxy anions ionized in PAA molecules depress the electrolytic dissociation of the carboxy groups around the anions^{5,6}, that is, the carboxy anion in the PAA molecule has an electrostatic potential. In this study, the PAAs with various MMWs were investigated. The pH curves of the PAAs without Ca^{2+} were higher than that of isobutyric acid and were not dependent on the differences in the MMWs of the PAAs (Fig.1). Isobutyric acid is a model molecule as a monomer unit of a PAA⁵ and the pH curve

showed a typical titration curve of an organic acid.

In the presence of Ca^{2+} , all curves of the PAAs with up to 40×10^4 MMW were the same as that of isobutyric acid and were not dependent on the content of Ca^{2+} and the MMW of the PAAs (Fig.2). However, the curve of the PAA with 100×10^4 MMW was affected by the content of Ca^{2+} . In the content of 8 mmol of Ca^{2+} , the curve of the PAA moved toward the low volume of the NaOH, and this phenomenon was reported by Iioka et al⁷. When the concentration of the PAA with 35×10^4 MMW was 8×10^{-3} M and the concentration of Ca^{2+} was 16 mM, the end-point of the curve of the PAA moved to a low value of NaOH (Fig.3). It is considered that unreactive carboxy groups exist in the aggregates formed by PAA and Ca^{2+} , and the number of the carboxy groups was altered by the molecular weight of a PAA and the concentration of Ca^{2+} and PAA. The aqueous solution of a PAA was used in this study, but the solution of 40 weight % of a PAA in clinical application is used as a cement liquid. The hardened cement prepared with the liquid containing high concentration of PAA contains a number of unreactive carboxy groups, and the carboxy groups affect the mechanical property of the hardened cement.

The addition of Al^{3+} had no effect on the titration curve. This is because the stability constant ($\text{p}K_c$) of $\text{Al}^{3+}/\text{OH}^-$ complex ($\text{p}K_c=9.0$) is larger than that of $\text{Ca}^{2+}/\text{OH}^-$ ($\text{p}K_c=1.6$)⁸, or that of $\text{Al}^{3+}/\text{PAA-COO}^-$ (carboxylic anion of PAA) may be small compared with that of $\text{Ca}^{2+}/\text{PAA-COO}^-$, and otherwise the solubility product ($\text{p}K_{sp}$) of $\text{Al}^{3+}/\text{PAA-COO}^-$ compound may be small compared with that of $\text{Ca}^{2+}/\text{PAA-COO}^-$. No aluminum hydroxides precipitated in the pH below 9 ($\text{p}K_{sp}$ of aluminum hydroxide : 3.1×10^{-18}).

The fact that the interaction between Al^{3+} and PAA-COO^- is small is of interest in studying the behavior of Al^{3+} in the hardening glass-ionomer cement.⁹

2. Binding ratio of the carboxy groups and Ca^{2+}

In the titration curve of the PAA with 35×10^4 MMW (4 mM, 50 ml (0.2 mmol)) with NaOH in the presence of Ca^{2+} , the concentration of Ca^{2+} linearly decreased, and the line bent at the end-point (Fig.5). The difference in the concentration of Ca^{2+} between its initial value and the end-point was 1.92×10^{-3} M and the decreased Ca^{2+} binded to PAA anion in the solution. Therefore, the amount of Ca^{2+} was about 0.1 mmol and was half that of the carboxy groups in the PAA solution. It was found that the binding molar ratio of the carboxy group and Ca^{2+} was about 2:1.

A mixture of the PAA (5 mM, 40 ml (0.2 mmol)), NaOH (0.05 M, 2 ml (0.1 mmol)) and 8 ml of H_2O was titrated with 0.05 M $\text{Ca}(\text{NO}_3)_2$ (Fig.6). The amount of NaOH added was 0.1 mmol and was half that of the carboxy groups in the PAA solution. The carboxy anions produced by neutralization of the PAA with NaOH was 0.1 mmol and react with Ca^{2+} in the solution. As a result of the reaction, the electrostatic potential in the PAA molecule decreases, that is, pH in the solution decreases. The bending-point of pH curves in Fig.6 shows that all of the produced carboxy anion binded to Ca^{2+} . The amount of the binded Ca^{2+} was about 0.05 mmol that was calculated from the volume of $\text{Ca}(\text{NO}_3)_2$ at the bending-point, and was half the carboxy groups (0.1 mmol) that were not neutralized with NaOH.

The binding molar ratio of the carboxy anion and Ca^{2+} was about 2:1 under the two aqueous solution system in this study mentioned above, and not dependent on the molecular weight of the PAA.

On the other hand, in a similar system to this study, the report states that the carboxy anions binded to Ca^{2+} rapidly decreased near equivalence point⁷⁾. According to the measurement of the concentration of free Ca^{2+} in the solution in this study, it is difficult to consider that the carboxy anions binded to Ca^{2+} decrease.

In the report, on the basis of some assumptions

that the electrostatic potential of the carboxy anion in the PAA was dependent on the charge density of the anion and is not dependent on the number of Ca^{2+} and apparent acid dissociation constant of a PAA is unaltered, the number of the carboxy groups binded to Ca^{2+} was calculated⁷⁾. But Fig.6 indicates that apparent acid dissociation constant changes with the amount of Ca^{2+} in the solution, and it is obvious that the electrostatic potential of the carboxy anion is dependent on the presence of Ca^{2+} .

3. Precipitation reaction of PAA and Ca^{2+}

The precipitation reaction of the PAA and Ca^{2+} occurred, and the concentration of Ca^{2+} is inversely proportional to that of OH^- (Fig.7). We considered the validity of the curve. The solubility product for the PAA/Ca precipitates and the equilibrium in the solution are shown below. Where K_{sp} , K' and K_w represent the solubility product of the PAA/Ca, the apparent acid dissociation constant of a PAA and ion product of water, respectively.

$$K_{sp} = [\text{PAA}^-] * [\text{Ca}^{2+}] \cdots \cdots (1)$$

$$K' = [\text{PAA}^-] * [\text{H}^+] / [\text{PAA}] \cdots \cdots (2)$$

$$K_w = [\text{H}^+] * [\text{OH}^-] \cdots \cdots (3)$$

The equation (4) is obtained from equation (1), (2) and (3). As the $[\text{PAA}]$ is experimentally determinable, the right hand side of the equation (4) is constant and the $[\text{OH}^-]$ and $[\text{Ca}^{2+}]$ shows an inversely proportional relationship.

$$[\text{OH}^-] * [\text{Ca}^{2+}] = (K_{sp} * K_w / K') / [\text{PAA}] \cdots \cdots (4)$$

The K' of the PAA was calculated from pH of half equilibrium point of the titration curve of the PAA, because the titration curve of a PAA in the presence of Ca^{2+} was the same as that of an organic acid. And the value was 1.97×10^{-5} .

The concentration of the PAA in the experiments was 0.004 M. The K_{sp} values were calculated by substituting those values and $[\text{OH}^-]$ and $[\text{Ca}^{2+}]$ values in Fig.7 to equation (4). The mean K_{sp} value at pH 4.67 was 3.56×10^{-6} .

4. Tensile bond strengths of the cements using

the PAAs

Tensile bond strengths of the cement using the PAAs with various MMWs to stainless steel became maximum at a MMW of about 15×10^4 (Fig.8)¹⁰. The reduction in the strength of the cements using PAA with a higher MMW may be due to the existence of unreacted carboxy groups in the cements. On the other hand, the PAA with a low MMW combined satisfactorily to calcium ion compared with the PAA with a high MMW, but the bond strength of the cements using PAA with a low MMW decreased. It was thought that the PAA molecules was apparently not available as binder among the particles of the cement powder because of the small and/or short size of the molecule. The decrease of the bond strength may be due to the mechanical properties of the hardened cement itself.

References

- 1) Smith, D. C. :A new dental cement, Brit Dent J., 125, 381-384,1968
- 2)Beeth,D.R. :A spectroscopic study of the interaction between human tooth enamel and polyacrylic acid (polycarboxylate cement), Archs orals Biol., 17, 907-911, 1972
- 3)Kubota, M., Araki,Y., Kitade, H., Iioka,A., Odachi,T., Ibaraki, Y., Matsuda,K., and Ohno, H: Studies on mechanism of adhesion of polyelectrolyte cements to human tooth, Part.1 Reactivity of cements liquid with human tooth and hydroxyapatite at their interface. 31 (5), 1389-1396, 1988
- 4)Kurata, S., Fujihara, T. and Negishi, H.:Stability constant of barium phosphoric acid complexes, Bulletin of Liberal Arts and Sciences, Kanagawa Dental College, 7, 105-109, 1989
- 5)Sakaguchi,Y., Tamaki,K., Murakami,T.: Potentiometric Titration of copolymers of acrylic acid or methacrylic acid, Kobunshi Kagaku, 27, 747-752, 1970
- 6)Chang, D. M.: The binding of free calcium ions in aqueous solution using chelating agentsphosphates and poly(acrylic acid), JAOCS, 60(3), 618-622, 1983
- 7)Iioka, A., Araki, Y., Matsuda, K. and Ohno, H.: Adhesion mechanism of polyelectrolyte cements to tooth structure-polyelectrolyte behavior of the cement polymers obtained by potentiometric titration in the presence of calcium ion, Dent Mater J... 8 (2), 236-242, 1989
- 8)Nihonkagaku-kai, ed., Kagakubinrankisohen II. Maruzen, 1984, p.II-346
- 9)S.Matsuya, T.Maeda, and M.Ohta: IR and NMR analysis of hardening and maturation of glass-ionomer cement. J Dent Res., 75 (12), 1920-1927, 1996.
- 10)Umemoto,K., Kurata,S. and Yamanaka,A.: The influence of molecular weight distribution of poly (acrylic acid) on tensile bond strengthof polycarboxylate cement, Bull of Kanagawa Dent Col., 18 (1), 29-32, 1970