DEVELOPMENT OF TECHNIQUE FOR DETERMINATION OF ANTI-SCALANT CONCENTRATION IN COOLING WATER SYSTEM

BY

MS. TIKUMPORN SUDSAKORN

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF MASTER OF
ENGINEERING (ENGINEERING TECHNOLOGY)
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ENTITLED

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ABSTRACT

AA/AMPs poly(acrylic acid:2-acrylamido-2-methylpropane sulfonic acid) and PMA (polymaeic acid) are an important anionic polymer that are used as an anti-scalant in water cooling system. It contained a negative charge that severally used to prevent a scale formation and also has a good dispersion efficiency. During cooling operation involving water evaporation, concentration, blow-down, and make-up water. The concentration of the antiscalant has to be monitored in order for optimum dosing. In this work, a simple technique to determine AA/AMPs and PMA concentration was developed using complexing agent to the polymer that can then form large cluster for light scattering enabling rapid turbidity measurement.

Here, benzethonium chloride or Hyamine, a large cationic molecule was used as a complexing agent for AA/AMPs and PMA to form a larger particle which can be detected via the UV-Vis spectroscopy technique. Turbidity was measured to confirm the complexation between these two types of chemicals. The result showed that Hyamine can be used for AA/AMPs and PMA concentration determination.

Keywords: Anti-scalant, cooling system, UV-Vis Spectroscopy

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Ms. Tikumporn Sudsakorn

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LIST OF SYMBOLS/ABBREVIATIONS

Symbols/Abbreviations	Terms
SIIT	Sirindhorn International Institute of Technology
TU	Thammasat University
EGAT	Electricity Generating Authority of Thailand
CAC	Critical aggregation concentration
CMC	Critical micelle concentration
HI	Hyamine
AS	Anti-scalants
Ca^{2+}	Calcium ion
AA/AMPs	Poly(acrylic acid:2-acrylamido-2-methylpropane sulfonic acid)
PMA	Polymaleic acid
PBTC	2-Phosphonobutane-1,2,4-tricarboxylic acid
AS-HI	Anti-scalant complexed with Hyamine
SO_4^{2-}	Sulfate ion

CHAPTER 1
INTRODUCTION

1.1 Statement of problem

Recirculating cooling water system is the process for heat exchanging. It transfers the hot water via the system. When waste heat is removed by evaporation, the remaining water in the system becomes more concentrated. Make-up water (raw water) that has many mineral elements (Ca^{2+}, Mg^{2+}, Silica etc.) is needed to add in the system in order to maintain the salinity, conductivity and prevent the cooling water from becoming too concentrated. The major problems in recirculating cooling water system are divided in 3 types e.g. scale formation, biofouling, and corrosion. The problem can affect the heat transfer and thermal exchange capacity inside the cooling system. Excessed heat can be occurred Therefore, the industry faces about cost, technique, and environmental impacts.

Scale formation is one of the major problems in a cooling system. Scales are hard deposited which stick firmly into the inner surface of the equipment inside the cooling system. When the huge amount of scale was occurred, off-line cleaning in the recirculating cooling water system was needed to perform in term of scale elimination. In addition, the company needs to construct the standby other heat exchangers in case of the stopped main one still cleaning and servicing, another one can be used for heat exchanging operation. That is a capital cost of company which is quite expensive cost. It is very important for design the cooling process to compensate the scale formation. Looking in more details of scale formation, the problem is not only occurred with the capital cost in the cooling system. Moreover, the problem will be correlated with the production line. A dropped in heat transfer efficiency can lead to reduce the performance of production process.

Anti-scalant is added in the recirculating cooling water system to prevent those serious problems that can occur when the system has a scale deposit. Many chemicals can be used as an anti-scalant or scale inhibitor depending on the purpose of using (Hasson, Shemer, & Sher, 2011). However, the optimum point of antiscalant concentration is needed to have a good efficiency to prevent a scale formation, reduce capital cost and the environment concern when its discharges to water resource. Many techniques are used for monitoring the amount of antiscalant such as potentiometric, fluorescent tracer, spectrometer etc. Inhibition step of anti-scalant is divided in three stages as follow (Pääkkönen, Riihimäki, Simonson, Muurinen, & Keiski, 2012);

1) Crystal modification; to prevent the building up of regular lattice and scale layer.
2) Crystal dispersion; to prevent the crystal accumulation due to increased anion.
3) Threshold inhibition makes the active crystal growth site are blocked.

Functionalized polymer can be used as the anti-scalant to prevent a scale formation in the recirculating cooling water system. PMA (polymaleic acid) is the macromolecules polymer that is used for mineral scale prevention especially for gypsum scale ($CaSO_4$) stabilization (Mohanty, Das, & Dhara, 2013). When use this polymer exceeded the optimum concentration, the problem is a salt formation with an alkaline earth metal ions or form micelle that retarded the scale prevention (Zahid Amjad & Koutsoukos, 2014; Martinod, Euvrard, Foissy, & Neville, 2008). AA/AMPs is called poly(acrylic acid:2-acrylamido-2-methylpropane sulfonic acid) is the copolymer that is used severally in the cooling system. This copolymer can be used in order to prevent a gymsum scale similar to the polymaleic acid. Moreover, some studies investigate that it is additionally used for calcium phosphate scale prevention and has a good efficiency for scale dispersion by testing with iron oxide dispersion (Z. Amjad, 2007).

Generally, the techniques for anti-scalant concentration determination are discussed about scale formation mechanism and in term of tagging fluorescence onto polymer. Some studies focus on turbidity measurement for determination. However, determination of more than one species of anti-scalant is not straightforward and normally requires elaborate techniques such as chromatography or fluorescence tagging.

Benzethonium chloride or Hyamine is the cationic surfactant that was used for many applications e.g. surfactant tritration (De Caro, 2014), extraction (Gundersen &

Jacobsen, 1968), and also used for determination anionic polymer concentration (J.D. Atlison, 1987). It had the potential to complex with other compounds or polymers that have an oppositely charge and generate a bigger cluster that can be measured by light scattering technique. Some studies mention in term of turbidity measurement.

In this study, it aims to develop the technique for concentration determination of AA/AMPs and PMA. These two chemicals are used as an anti-scalant that normally added in the cooling system to prevent a scale formation. The technique for anti-scalant determination is not widely use and not much studied especially in term of quantitative issue. Benzethonium chloride or Hyamine was a cationic agent that used for catching anion in the previous studies. Therefore, this study will aim to use Hyamine to form the complexation with two types anti-scalants. UV-spectroscopy for characteristic the spectra of each chemicals that react with Hyamine will be utilized for the concentration determination.

1.2 Research objective

1.2.1 To study the effect of Hyamine (cationic surfactant) to anionic Polymer (AA/AMPs, PMA).

1.2.2 To determine anti-scalant concentration (AA/AMPs, PMA) by using Hyamine.

CHAPTER 2
REVIEW OF LITERATURE

Recirculating cooling water system is the process for heat exchanging. It transfers the hot water via the recirculating cooling water system. When waste heat is removed by evaporation, water becomes more concentrated. The water used in cooling system was generally supplied by treating natural river water. After treatment, this water still contains certain amount of calcium ion, and it is used as a make-up water in the cooling system. The calcium ion becomes more concentrated as the water is circulated inside the cooling system basin. If the water is allowed to be very concentrated, some hard scales e.g. calcium scale can be formed in the cooling system and pipelines, blocking the water flow. Make-up water is needed to be added in the system in order to prevent the cooling water from becoming too concentrated. Then, the system recirculates water again for many times.

The major problems in this system divide in 3 types such as scale formation, biofouling, and corrosion. The problems affect to the heat transfer and the thermal exchange capacity in the system. Hence the industry needs a way to prevent scaling in cooling system (Chaussemier et al., 2015).

2.1 Scale formation

Scale formation is the major problem of cooling system. Scales are divided in two types, mineral scales, and colloidal inorganic species. Mineral scales are normally in the crystalline form such as $CaCO_3$, $CaSO_4$. For colloidal scale, the amorphous aggregates from silica that occurred in the cooling system and hard to prevent, because it forms as amorphous form (Demadis, Mavredaki, Stathoulopoulou, Neofotistou, & Mantzaridis, 2007).

2.2 Mineral scale formation

Mineral scales are usually occurred in the crystalline form such as $CaCO_3$, $CaSO_4$. There are 3 stages to form the mineral scale e.g. 1) supersaturated 2) nucleation 3) crystal growth. – 1) crystal modification; to prevent the building up of regular lattice and scale layer 2) crystal dispersion; to prevent the crystal accumulation due to increased anion charge and 3) threshold inhibition makes the active crystal growth site are blocked (Chaussemier et al., 2015), (Pääkkönen et al., 2012).

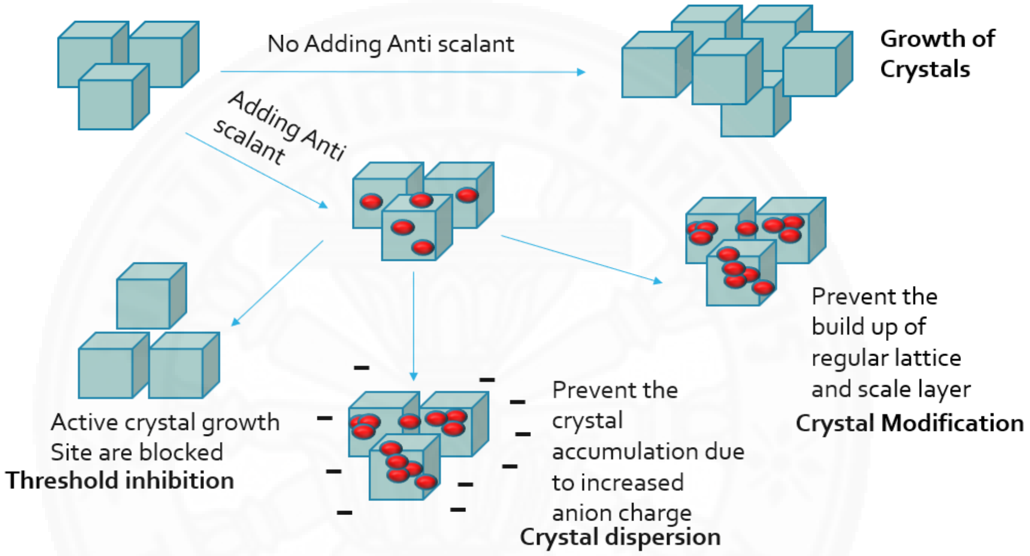


Figure 2.1 Schematic of mineral scale inhibition

2.3 Amorphous silica

Silica is a one of amorphous forms of colloidal scale that is generally occurred in the cooling system. It is needed to add anionic charge to prevent a scale formation. Amorphous silica is generated by soluble silica in the system. It is the part of silicate (or silicic acid) and various types of silicate deprotonation depended on pH. Silicate is performed as unionized $Si(OH)_4$ at pH below 9. above pH 9, ionized silica such as $SiO(OH)_3^-$ or $SiO_2(OH)_2^{2-}$ are performed. Amorphous form of silica will be occurred at pH 6 to 10. Normally, the water system of industry has pH 7 to 10, which there are ionized, and unionized silica were occurred in the water. (Zhang, Xin, Chen, & Li, 2012).

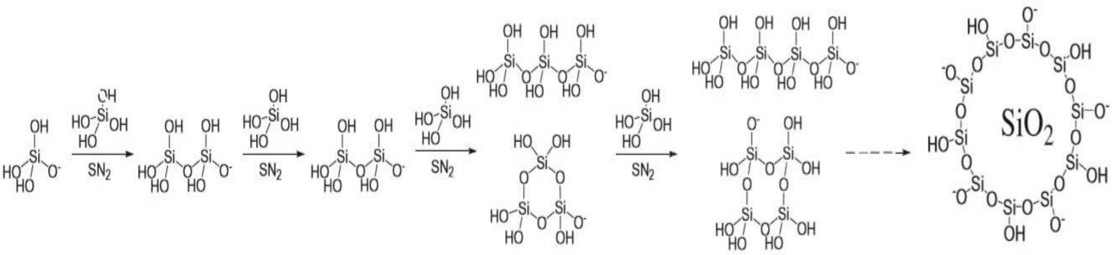


Figure 2.2 Schematic of Amorphous forms of silica

2.4 Anti-scalants

Anti-scalants needs to add in the cooling system to prevent a scale formation. Popular anti-scalants were polyphosphate, polyphosphonate, polycarboxylate that still using in recent year for scale prevention (Yang, Liu, Gu, Ding, & Shen, 2001).

2.4.1 AA/AMPs

AA/AMPs is the copolymer between acrylic acid (Called AA), and 2-acrylamido-2-methyl-propano-sulfonic acid (Called AMPs). AA is known as its cheap and AMPs is able to dissolve in the water (Rosa, Bordado, & Casquilho, 2002). Pka of AA/AMPs were 3.2 and 4.2 for sulfonic group and carboxylic group, respectively. (Atta, El-Mahdy, Al-Lohedan, & Abdullah, 2015)

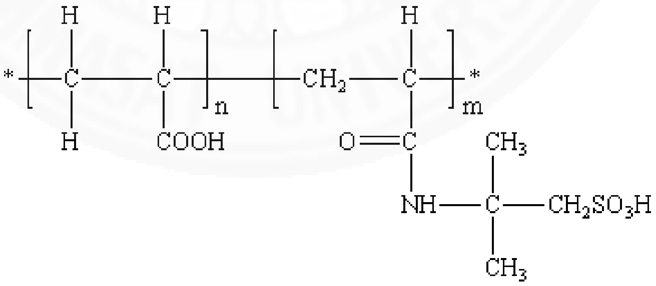


Figure 2.3 Structure of AA/AMPs

2.4.2 PMA

PMA or polymaeic acid is a macromolecules polymer that used in water treatment process for gypsum surface absorbent. It is an anionic polymer that contained carboxylate group in the chain (Mohanty et al., 2013).

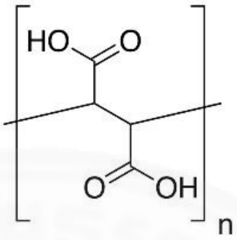


Figure 2.4 Structure of PMA

Normally, Anti-scalant are the formed of inorganic phosphonate and phosphate which are known as a secondary pollutant. They are released to the water resource then environmental problems can be occurred such as eutrophication because they are non-biodegradation (Chaussemier et al., 2015), (Ketsetzi, Stathoulopoulou, & Demadis, 2008).

Biofouling attachment can be induced by polyacrylate acid based-antiscalant in term of initial bacterial attachment on to a surface of RO system. They generated the attachment of bacterial by increasing membrane hydrophobicity and modification of membrane physico-chemical properties. Biofilm can be induced on the surface of membrane by polyphosphonate based-antiscalant. It is directly correlated with phosphorous consuming of organism (Sweity et al., 2015).

2.5 Techniques for anti-scalant concentration determination

In recent year, the techniques for determination anti-scalant concentration in cooling system are interested in term of control the chemical concentration and operating cost. Normally the anti-scalant concentration is estimated based on the initial concentration dose, the number of cycles of the circulated water in the cooling system to get the last concentration of anti-scalant that remained in the cooling system. However, it is the estimate value. A Fluorescence tag onto anti-scalant was widely used for this field. Fluorescence tag techniques that was developed along with many types of anti-scalants were patent issued by numerous research fields (Rasimas, 2001; YOUNG, 2019a, 2019b, 2019c). They used the principle of luminescence of the fluorescence chemical tagged to know the amount of anti-scalant in the system (M. Oshchepkov & S. Tkachenko, 2019). On the other hand, this technique had to change all types of chemical to become a fluorescence material. The cost of the anti-scalant polymer will be increased, although it can reduce the cost of using under or over-amount of the anti-scalants.

Another technique, potentiometric method also be used for PA (Polyacrylate) concentration determination in cooling system via copper ion-selective electrode by adding Cu^{2+} to complex with PA. This technique can measure ‘free’ or ‘effective’ polymer that still distort the morphology of scale in the cooling system (Yuchi, Gotoh, & Itoh, 2007).

However, there were few of studies for anti-scalant monitoring in term of two types of polymers in the cooling system. Colorimetric method was introduced for polycarboxylates and/or sulfonates determination in aqueous system by colour development between anionic polymer and cationic dye complexation. pH was the key factor for separation between these two types of polymers. pH adjusted less than 3 was used for sulfonate determination and between 3 to 12 was used for polycarboxylate determination. Sulfonate group was a strong acid more than carboxylate, that can be protonated pH as low as 2.5. In contrast, carboxylate protonation cannot occur in this pH range due to there are few of charges protonation compare with sulfonate. Dyes’ types also selected for suitable determination with specific types of polymers. The absorbance of complexed polymer with dye was measured via spectrophotometer (300 nm-700 nm). Concentration of polymer can get from standard curve comparison (Ronald R. Myers, 1990).

From other studies, NUUTINEN, LEHMUSTO, SHVONEN and MUNDILL (2015) used Lantanide (III) ions to determine one or more components of anti-scalants in the oilfield. The principle was an excitation the molecules of ionized polymer that reacted with Lantanide (III) ions. Then, luminescence of total concentration of polymer was measured via the time-resolved luminescence technique. The specific excited wavelength was then measured. In case of having three components anti-scalants – if the third component was a fluorescence tagged polymer, it was measured via specific fluorescent signal directly. The concentration of three types of anti-scalants were got from the algorithm or mathematic relation (NUUTINEN, LEHMUSTO, SHVONEN, & MUNDILL, 2015).

2.6 Benzethonium chloride (Hyamine 1622)

Benzethonium chloride or Hyamine is a cationic surfactant that has a positively charge on molecule. It is a quaternary ammonium salts that contains hydrophobic tail and hydrophilic polar head. Normally, Hyamine can be used for many applications i.e. cationic titration (De Caro, 2014), extraction (Gundersen & Jacobsen, 1968), and determination anionic polymer (J.D. Atlison, 1987).

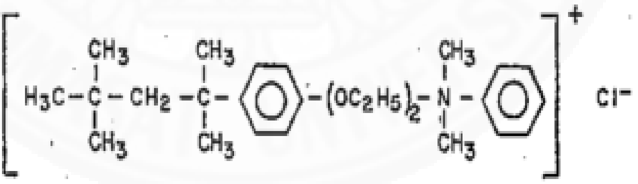


Figure 2.5 Benzethonium chloride or Hyamine

De Caro (2004) reported about an anionic surfactant titration for METTLOR TOLEDO titrators that was a technique for SDS concentration determination by using Hyamine or benzethonium chloride as a complex simple matrix. Turbidity will be generated by anionic-cationic surfactant complexation. The equivalent point was determined when turbidity was reached to maximum. Light transmission was measured after a complexation had occurred in the system. Using excess titrant caused a dropped of turbidity, precipitate will be dissolved in water again. Anionic surfactant concentration can be determined by the equivalent point.

Gundersen and Jacobsen (1968) used Hyamine as a selective extraction agent for cobalt extract from cobalt-thiocyanate. Cobalt was formed as a complexed cluster with Hyamine. Muroxide was used as an indicator to form a blue precipitated. Hyamine can be dissolved in organic phase e.g. chloroform or benzene. The organic solvent was a phase for cobalt extraction that the blue precipitated can be dissolved in. Spectrophotometry was utilized for the measurement. The specific wavelength was selected at 624 nm.

Atlison, Wimberly and Ely (1987) studied the technique for determination of polyacrylamide and other anionic polymers by using Hyamine for the complexation. The study was analysed the brine water from oil field plant. Turbidity was measured after the complexation had occurred in the solution. The detection limit provided 0.5 ppm to 1 ppm for polyacrylamide.

2.7 Polymer-Surfactant complexation

Polymer-surfactant complexation is widely studied for various applications e.g. waste-water treatment (Letcher, Chu, & Smyth, 2020), pharmaceuticals (Chadha & Bagheri, 2019). The driven forces of the complexation were discussed about electrostatic and hydrophobic interaction. The electrostatic interaction was happened through the oppositely charge between polymer and surfactant. Hydrophobic interaction was discussed about the aliphatic tails of surfactant (J. Koetz & Kosmella, 2007). The polymer-surfactant system can be affected with various factors. e.g. charge density, concentration of polymer or concentration of surfactant (Bain et al., 2010). The interaction between charge polymer and oppositely charged surfactant is considered as the strong interaction which had critical aggregation concentration (CAC) of polymer-surfactant system much lower than critical micelle concentration (CMC) of pure surfactant system (Diamant & Andelman, 2000).

2.7.1 Surfactant morphology

Surfactant morphologies depended on concentration. Aferni, Guettari, Kamli, Tajouri and Ponton (2020) studied the morphologies of surfactant by using the electric conductivity measurement for structural transition of surfactant. Various concentrations of AOT or sodium bis (2-ethylhexyl) sulfocinate were measured the assembly when its dissolved in the water. Electric conductivity was measured through the solution. Then, extrapolation of logarithm of conductivity (Ω) and AOT concentration were plotted to observe the correlation of these data. The result showed that critical AOT concentration was separated in three regions. Figure 2.6 showed the difference slopes of AOT at difference concentrations. Slopes were divided in three regions that were observed through the electric conductivity change. The first region was discussed in term of surfactant monomer. Then, spherical micelle morphology was occurred at the second regime. Critical micelle concentration was called at the transition of region one to two. Increasing the concentration of surfactant again leaded to form a cylindrical morphology (El Aferni Ahmed, Guettari Moez, Kamli Marwa, Tajouri Tahar, & Alain, 2020).

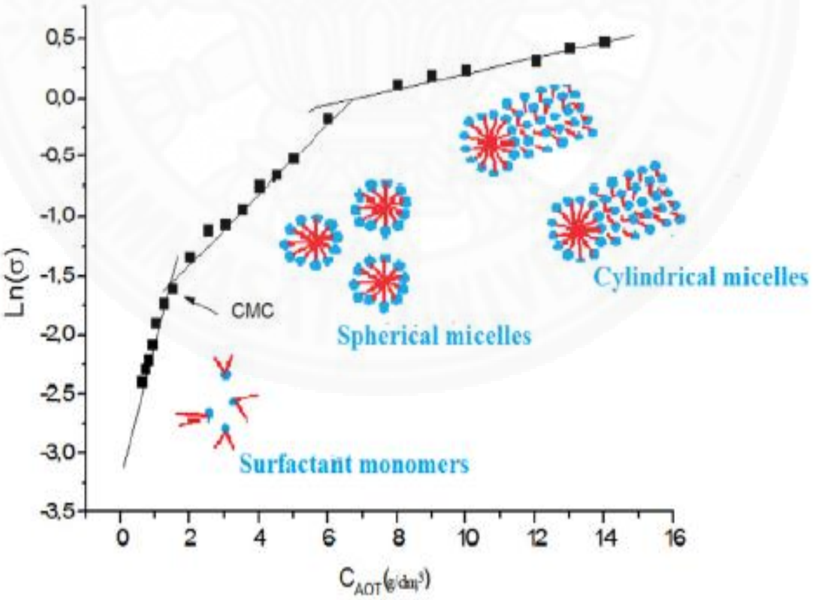


Figure 2.6 The extrapolation of logarithm of conductivity (Ω) and AOT at difference concentrations

Jasmine Chadha & Ahmad Bagheri (2019) studied the critical micelle concentration of Hyamine 1622 or benzethonium chloride by using specific conductivity measurement. They dissolved the surfactant in deionized water at various concentrations of Hyamine. Specific conductivity was then collected for each concentration. The result showed that benzethonium chloride or Hyamine 1622 had the critical micelle concentration at 0.00322 mol/L (1,500 ppm) (Chadha & Bagheri, 2019). In order to use surfactant complexed with oppositely charged polymer, the binding isotherm starting was observed at critical aggregation concentration (CAC) that was lower than critical micelle concentration (CMC) in polymer free surfactant solution.

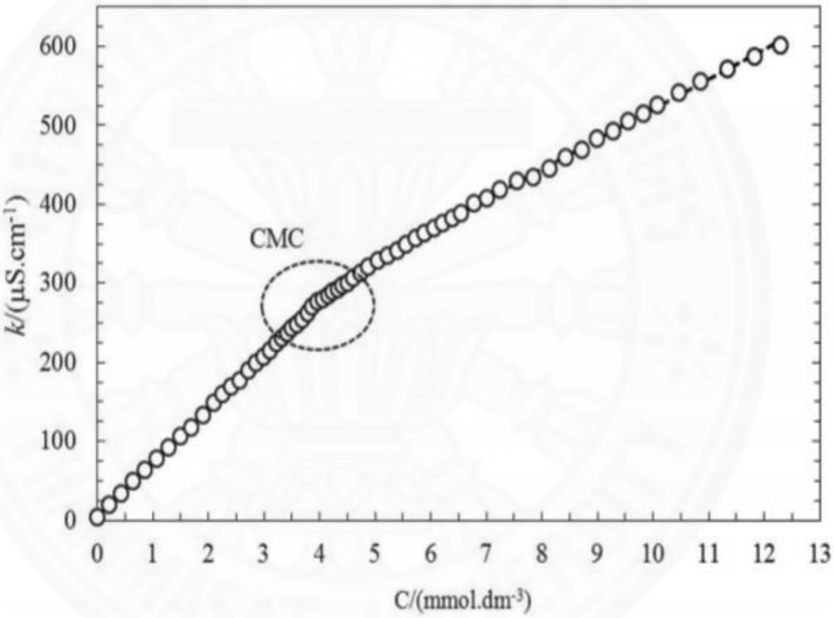


Figure 2.7 Schematic representation of the critical micelle concentration of Hyamine

2.7.2 Partial collapse of polymer-surfactant system and the multichain complexes

Polymer chain will be extended when its dissolved in the water due to electrostatic repulsion of charge along with the chain of polymer. Increasing polymer concentration results in more viscous of solution. The collapse of polymer chain will be occurred when adding oppositely charged surfactant in the system. The complexation of polymer with oppositely charged surfactant occurs at surfactant critical aggregation concentration (CAC) that lower than critical micelle concentration (CMC) of surfactant. When the collapses are occurred, polymer chains are shrinking or coiling because surfactant can neutralize the extended chain of polymer. This result affects the coil size decreasing that induced the chain dimension decreasing. As the result, the polymer chain can be formed more multichain complexes. Herein, this step can increase the size of particle. Stage of partial collapse and multichain complexes were not easy to observe except the case of CAC is much lower than CMC (Diamant & Andelman, 2000).

2.7.3 Binding mechanism

The binding mechanisms is divided in two parts; (1) Non-cooperative binding, (2) Cooperative binding. Non-cooperative binding is occurred at the very low concentration of surfactant where the binding sites of polymer are not ready to fulfill with surfactant. For cooperative case, the binding sites of polymer are ready to bind with the surfactant molecules. The binding process is related to thermodynamic aspect. Enthalpy is discussed for binding process along with increasing surfactant concentration (Guzmán et al., 2016).

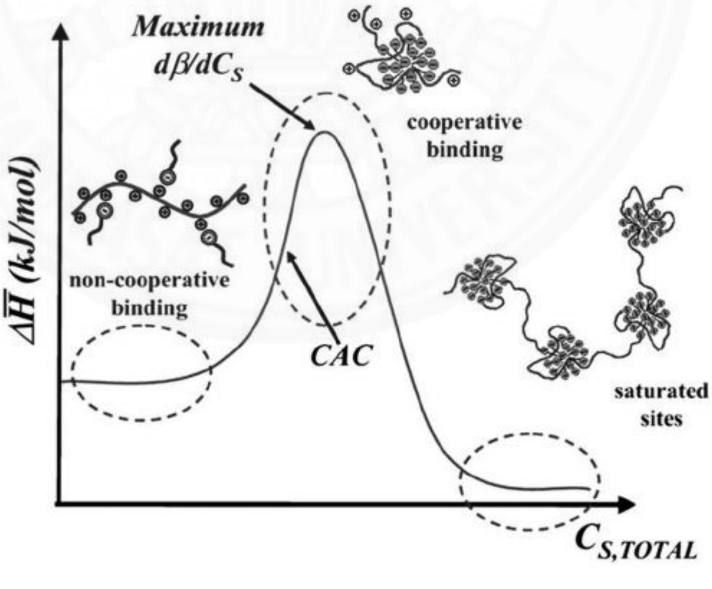


Figure 2.8 Schematic representation thermodynamic dependence on surfactant concentration (CS,TOTAL) for complexation between polymer and surfactant system

Figure 2.8 showed that the first regime represented the non-cooperative binding process when using the low surfactant concentration. Enthalpy (ΔH) is then raised with increasing surfactant concentration where the binding sites of polymer are ready to bind with surfactant molecules. β was represented a degree of binding between surfactant molecules and polymer. Consequently, enthalpy is reached to maximum value where the polymer binding sites are fulfilled with surfactant molecules completely. The later decrease can be discussed in term of re-solubilization of the complexed particles. This case can be interpreted in term of binding site of polymer is saturated by surfactant molecules and the free micelle molecules of surfactant are formed at the surface of the complexed cluster.

2.7.4 Formation of micelle-like structure in polymer-surfactant system

The charge of polymer attached to head group of oppositely charged surfactant. Electrostatic attraction is the driven force for this interaction. Increasing surfactant concentration reaches to critical aggregation concentration (CAC), a micelle-like structure is formed in the system by hydrophobic tail of the surfactant in the core and hydrophilic head group of the surfactant attaches to oppositely charged polymer. Partial collapse or the instabilization of polymer chain will occur at the CAC point of the polymer-surfactant binding. It was induced by the interaction between two species of polymer and surfactant overcome the intinction of intrachain repulsion of the polymer. Charge neutralization is occurred with the enough charge of surfactant. Precipitate will be generated at the neutralized charge system. Further increased surfactant concentration above the neutralize phase leads to resolubilize of the complexation. In this case, hydrophobic tail of surfactant attaches to the neutral complexed particle that was formed in the precipitate while the hydrophilic head group attaches with water (Khan & Brettmann, 2018). Subsequently, the second layer is formed at the surface of the complexed particle. Due to polar head is attached to the water, the particle can be redissolved in water again.

In this study, the technique to measure concentration of the anionic anti-scalant polymer AA/AMPs and/or PMA through the complexation with a positively charged

Hyamine molecule will be developed. The complexation results in an increased light scattering or absorbance which can be monitored using UV-Vis spectrometer and calculated the coefficient allowing for the polymeric anti-scalant AA/AMPs and/or PMA concentration to be determined.

CHAPTER 3
MATERIALS AND METHODS

3.1 Materials

Stock solutions 1,000 ppm of polymaleic acid homopolymer (PMA, 50% active), acrylic acid-2-acrylamido-2-methylpropane sulfonic acid copolymer (AA/AMPs, 40% active) and 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC, 50% active) prepared as product followed the instruction of Electricity Generating Authority of Thailand (EGAT). The word ‘as product’ means the concentration is calculated based on the amount of the AS product weighed out, as the actual polymer concentration in the AS commercial product is not known. The concentration is calculated from the amount of the anti-scalant product weighed out regardless of their advertised, or specified concentration (typically 50% polymer content specified on the label). The benzethonium chloride (Hyamine®, 1622 reagent) was purchased from Sigma Aldrich and also prepared as product.

Firstly, Characteristics of water sample were studied in term of calcium ion concentration, pH, and turbidity. The anti-scalant concentration determination was carried out by using Hyamine mixed with anti-scalant. Study the effect of time for reaction and Hyamine concentration have been focused. Simultaneously, the complexed particles were characterized by zetasizer in term of particle size and zeta potential. Next, study the effect of calcium ion concentration was then conducted with various concentrations of Ca^{2+}. Test of interference was tested with PBTC anti-scalant and sulfate. Finally, the development technique was used for anti-scalant concentration determination that contained in the water samples (Figure 3.1).

Water properties

- Calcium Ion concentration
- Turbidity and pH measurement

Complexation of HI (Hyamine) with AS

UV-Vis and turbidity measurement

- Effect of time for complexation
- Effect of Hyamine concentration complexed with difference two types of anti-scalant

Characterizations of AS-HI by nanosizer

- Zeta potential
- Particle size

Effect of calcium ion concentration

Test of interferences

- Effect of PBTC to the development technique
- Effect of sulfate to the development technique

Determination of AS concentration

in water samples

Figure 3.1 The experiment set up and procedure

3.2 Water properties

3.2.1 Calcium ion concentration

The calcium concentration in the water samples was determined using an inductively-coupled plasma spectrometer (ICP). The water sample was filtrated using a 0.22 µm Nylon filter

Calibration curve was constructed using a 500 ppm stock solution of $CaCl_2$ (180 ppm of Ca^{2+}). The solution was diluted 2.5, 5, 10, 15, 20 times. The ICP measurement was conducted using the specific Ca^{2+} emission wavelength at 317.93 nm. Two types of water were used in this work which are: (1) the make-up water (treated raw water used for re-filling the cooling water in the power plant), and (2) the actual recirculating in the cooling basin system, or the basin water.

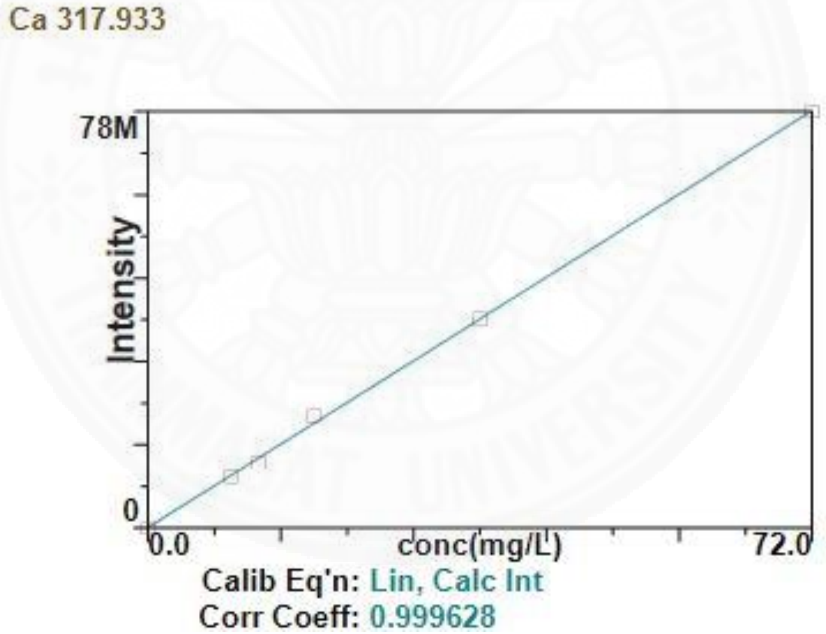


Figure 3.2 Show the standard curve of calcium ion concentration measured using ICP

3.2.2 Turbidity and pH measurement

Turbidity of water sample was measured via a turbidity portable meter (Hach 21000Q). The measurement method based on ratio turbidimetric determination using ratio of a primary nephelometric scattered light signal (at 90 degree) to the transmitted scatter signal (EPA Method 180.1). pH was measured via a pH probe measurement.

3.3 Complexation of HI (Hyamine) with AS

Benzethonium chloride (Hyamine®, 1622, Hyamine or HI hereafter) was used for anti-scalant (AS hearafter) determination by forming complexation between anti-scalant (negatively charged) and the Hyamine (positively charged). The experiments were conducted as below;

3.3.1 Effect of time for complexation

The reaction time for complexation was varied in order to observe the optimum time for the complexation between the anti-scalant and the oppositely charged of surfactant. AA/AMPs at 20 ppm as product was mixed with HI at 100 ppm to obtain the complexation without stirring. UV-Vis spectrophotometer equipped with dip-probe was used for the absorbance observation. The development of absorbance was collected every minute until 40 minutes a plotted as a function of time.

3.3.2 Effect of HI concentration

Stock solution of HI was prepared as product. The word ‘as product’ means the concentration is calculated based on the amount of the AS product weighed out, as the actual polymer concentration in the AS commercial product is not known. The concentration is calculated from the amount of the AS product weighed out regardless of their advertised, or specified concentration (typically 50% polymer content specified on the label). The procedure was prepared by weighting 0.1 g of HI in deionized to dissolve the chemical. Final volume of this mixing was adjusted to 100 ml to get the stock solution of HI 1,000 ppm as product. Various concentrations of the surfactant were prepared by using equation (3.1).

$$C_1V_1 = C_2V_2 \tag{3.1}$$

where;

C_1 = Concentration of HI stock solution (1,000 ppm)
V_1 = Volume of stock solution (mL) obtained from calculation
C_2 = Concentration of HI in the final system (ppm)
V_2 = Total volume of solution in the complexation system (20 mL)

Various concentrations of AS were also prepared as product same as stock solution of HI (0.1 g of chemical in 100 mL solution). The concentrations of AS were prepared in 4 concentrations by pipetting stock solution 1,000 ppm as product of AS to 0.5 ml, 1 mL, 1.5 ml and 2 ml. The solution was prepared using make-up water as the mixture. The total volume was then adjusted to 100 ml in volumetric flask to obtain the final AS concentrations of 5 ppm, 10 ppm, 15 ppm and 20 ppm, respectively. The use of make-up water in the mixing procedure was to simulate the same situation as that in the actual recirculating cooling water system.

Mixing procedure was considered as a simple mixed for AS-HI complexation by pipetting stock solution of HI to mix with each concentration of AS directly. The turbidity or UV-Vis measurement were taken 10 minutes after mixing. For UV-Vis absorbance, the spectrum was taken over 190-600 nm, with 1 nanometer resolution. The absorbance at 320 nm was chosen to be used in the calculation due to light scattering from the complexed particles. For turbidity, a portable turbidity meter was used. Various concentration of HI surfactant (50 ppm, 100 ppm, 300 ppm and 500 ppm) were prepared as Table 3.1.

The plot between absorbance and concentration of AS with various concentrations of HI was constructed to observe the relation between these two parameters.

Table 3.1 Preparation condition of various HI concentration

[HI], (ppm)	Volume of HI (ml)	AS (ml)
50 ppm	1 ml	19 ml
100 ppm	2 ml	18 ml
300 ppm	6 ml	14 ml
500 ppm	10 ml	10 ml

3.4 Characterizations of AS and HI

Various concentrations of HI were prepared to 50 ppm, 100 ppm, 200 ppm, 300 ppm, 400 ppm, 500 ppm, 600 ppm and 700 ppm for polymer-surfactant complexation. The AS concentration of both AA/AMPs and PMA were fixed the concentration at 20 ppm in the make-up water solution as a single component analysis. After mixing, the reaction was allowed to proceed for 10 minutes without stirring. Zeta potential and turbidity were then measured. The experiment was investigated the suitable surfactant concentration to form the complexation with anti-scalant.

Subsequently, Various concentrations of AS were prepared at 5 ppm, 10 ppm, 15 ppm and 20 ppm as product. HI at 100 ppm and 300 ppm were then utilized as surfactant for complexation to observe the effect of polymer concentration.

3.4.1 Zeta potential

Zeta potential was observed the charge on the surface of complexed particle by using zetasizer (Zetasizer Ver.7.11 Malvern Instrument Ltd.). Electrophoretic Light Scattering (ELS) is the technique to measure zeta potential of particle.

3.4.2 Particle size

Particle size of the complexation was collected by using zetasizer machine (Zetasizer Ver.7.11 Malvern Instrument Ltd.). Dynamic light scattering (DLS) principle was used to analyze the particle size. The temperature was controlled at 25.0 ± 0.05 ºC.

3.5 Effect of calcium ion concentration

Calcium cations presenting in the water can compete with the HI molecule for binding with the AA/AMPs, hence the concentration of calcium ion may also affect the turbidity development. This experiment was conducted to simulate the effect of calcium ion in the water. Various calcium ion concentrations (25, 50, 100, 200, 300, 400, 500 and 600 ppm) were added into the solution containing AA/AMPs at 20 ppm before the reaction with HI 100 ppm. The reaction was allowed to proceed for 10 minutes and the absorbance at 320 nm was measured.

3.6 Test of interferences

Several chemicals are typically employed in cooling system, verification of the interference of each chemical to the developed technique is needed to study the effect of other chemicals on the technique for determination of AS concentration.

3.6.1 Effect of 2-Phosphonobutane-1,2,4-tricarboxylic acid (PBTC) to the development technique

PBTC is another type of an anti-scalant that contained phosphorus in the chain, also used frequently together with AA/AMPs or PMA in the cooling system to prevent a scale formation. Experiment was conducted by using various concentrations of PBTC (0, 5, 10 and 20 ppm) mixed with HI 100 ppm with/and without AS e.g. AA/AMPs and PMA. The procedure is as follows:

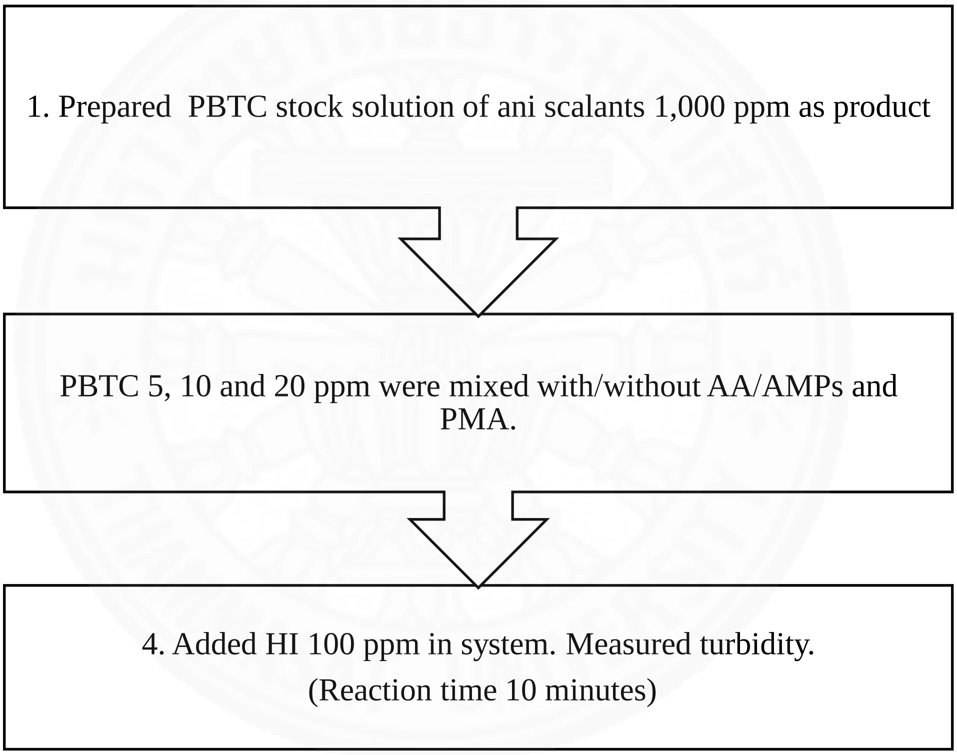


Figure 3.3 Method for testing the effect of PBTC with HI at 100 ppm to turbidity

Table 3.2 Conditions for PBTC interference testing

AA/AMPs (ppm)	PMA (ppm)	PBTC (ppm)
5	5	0
5	5	5
5	5	10
5	5	20

3.6.2 Effect of sulfate to the development technique

Sulfuric acid was utilized for pH adjust in the actual recirculating cooling water system. Sulfate ion (SO_4^{2-}) can be ionized from the process, hence, the experiment was conducted by using AA/AMPs at 20 ppm mixed with the synthetic water ([Ca^{2+}],100 ppm dissolve in DI water). Subsequently, HI (100, 300 and 500 ppm) was mixed and measured the turbidity after 10 minutes reaction time.

Various concentrations SO_4^{2-} (125, 250, 375, 500, 625, 875, 1000, 1500, and 2000 ppm) from the stock solution of Na_2SO_4 (10,000 ppm SO_4^{2-}) was then mixed with the AS-HI system above and investigated the effect of sulfate ion to the technique development.

3.7 AS concentration determination

The correlation of absorbances for each concentration of HI and AS concentration (AA/AMPs and PMA) can be used to calculate the amount of AS in the system by using HI at two concentrations to react with the two AS in the system. The calculation is based on linear relationship between the absorbance (or turbidity developed) and the amount of the AS polymer in the system. Normally, the absorbance measured at one HI concentration alone cannot be used to calculate the amount of each of the two AS polymer in the system. However, since each AS polymer responses differently to the HI, it is possible to use two concentrations of HI reacting with the sample of interest in order to calculate the amount of the two anti-scalant polymers in the system.

As the result, coefficient a1 of HI concentration at 100 ppm was calculated from spiked method with known amount of AA/AMPs concentration in water sample. Subsequently, coefficient a2 and b1 of HI concentration at 300 ppm was calculated from spiked method with known amount of AA/AMPs and PMA, respectively.

The specific wavelength from spectrometer was collected at 320 nm after the complexation time of 10 minutes.

At 100 ppm of HI complexed with AA/AMPs (the first AS polymer), the coefficient can be written as follow;

$$a1 = \frac{Y1-o1}{S1} \qquad (3.2)$$

where;

Y1 = absorbance of AA/AMPs reacted with HI 100 ppm (at 320 nm)

S1 = concentration of AA/AMPs

a1 = slope or coefficient variation of Y1 and S1

o1 = absorbance background at 320 nm

At 300 ppm of HI complexed with AA/AMPs, the equation is;

$$a2 = \frac{Y2-p1}{S1} \qquad (3.3)$$

where;

Y2 = absorbance of AA/AMPs reacted with HI 300 ppm (at 320 nm)

S1 = concentration of AA/AMPs

a2 = slope or coefficient variation of Y2 and S1

p1 = absorbance background at 320 nm

At 300 ppm of HI complexed with PMA, the equation is;

$$b1 = \frac{Y3-p2}{S2} \qquad (3.4)$$

where;

Y3 = absorbance of PMA reacted with HI 300 ppm (at 320 nm)

S2 = concentration of PMA

b1 = slope or coefficient variation of Y3 and S2

p2 = absorbance background at 320 nm

When the water sample containing the two AS at concentrations S1 and S2 (for AA/AMPs and PMA respectively) is mixed with HI at 100 ppm and 300 ppm concentrations and allowed for 10 minutes reaction time. The absorbances Y100 at 100 ppm and YT,300 at 300 ppm may be expressed as;

100 ppm HI; $Y100 = a1S1 + o1$ (3.5)

300 ppm HI; $Y300 = a2S1 + b1S2 + p_{avg}$ (3.6)

p_{avg} is the average value of background absorbance of the two types of AS (AA/AMPs and PMA) at concentration of HI 300 ppm.

According to Y300 needs to use for PMA concentration determination only. The absorbance of AA/AMPs at HI 300 ppm was subtracted from the system;

$$Y300_{PMA} = Y300 - (S1 \times a2) \qquad (3.7)$$

where;

$Y300_{PMA}$ = absorbance of PMA react with HI 300 ppm only (at 320 nm)

The calculation was extrapolated by using absorbance and coefficient of two polymer anti-scalants in the unknown water sample.

$$S1 = Y100/a1 \tag{3.8}$$

$$S2 = Y300_{PMA}/b1 \tag{3.9}$$

CHAPTER 4
RESULT AND DISCUSSION

4.1 Water properties

Table 4.1 showed characteristics of the make-up water and the water in the recirculating system. The make-up water has lower calcium ion concentration than the cooling water in the recirculating cooling water system (basin water) due to their circulation cycles in the system. Turbidity and pH have also increased after recirculation in the basin.

Table 4.1 Water characteristics

Sample	Calcium ion concentration (ppm)	Turbidity (NTU)	pH
Make-up water	26.50	2.92	8.35
Water in the cooling system (Basin water)	164.80	14.33	9.45

4.2 Complexation of HI (Hyamine) with AS

4.2.1 Effect of time for complexation

This experiment was conducted to confirm the time for complexation between polymer and HI. According to this technique was developed for a monitoring system to determine an anti-scalant concentration in the cooling system, minimize time was suitable for the operation. In this study, the complexation was set by using AA/AMPs at 20 ppm. Absorbance data was then measured every minute until 40 minutes to find an optimum time for the development technique.

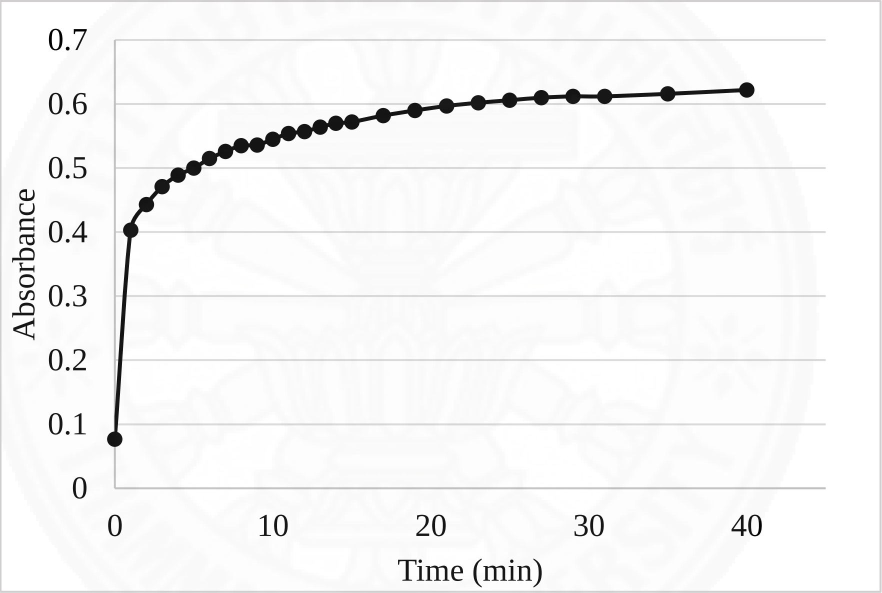


Figure 4.1 Absorbance development (at 320 nm) with time (min); AA/AMPs 20 ppm, HI 100 ppm

Figure 4.1 showed that initially the absorbance increased rapidly and increased with increased time for complexation until about 40 minutes. After 10 minutes, the absorbance increased only slightly until 40 minutes. To compromise between the measurement time and the complexation time, the complexation time of 10 minutes was selected as the optimum time for practical operation.

4.2.2 Effect of HI concentration

Various concentrations of HI at 50 ppm, 100 ppm, 300 ppm and 500 ppm were tested in order to find a suitable range of surfactant concentrations for reaction with the AS.

At 50 ppm HI, the absorbances of mixture were observed not to change significantly, even with a higher concentration of AS for complexation as shown in Figure 13 and 14. It also does not show good linear response. The R-square has quite a low value (AA/AMPs = 0.4201, PMA = 0.0299).

The higher concentration of HI yields better, linear correlation as shown in the Figure 4.2 and 4.3. The rate of absorbance increased with increased AS concentrations are also different between the two polymers. At 100 ppm HI concentrations, absorbance and turbidity increased more rapidly with increased AA/AMPs concentrations than with increased PMA concentrations.

However, at 300 and 500 ppm HI, the absorbance increases almost at the same rate for both AA/AMPs and PMA increased concentrations. It should be noted that for AA/AMPs, using 500 ppm HI yields lower absorbance value than using 300 ppm HI.

Figure 4.4 showed that, at the same concentration of polymer, increasing HI concentration can lead turbidity increasing. The rate of turbidity increases quite similar to that of the absorbance. At 500 ppm HI, the turbidity starts to decrease, the effect which will be discussed in section 4.3.1.1. Thus, HI concentration at 300 ppm was selected for reaction with the AS to develop maximum turbidity for measurement.

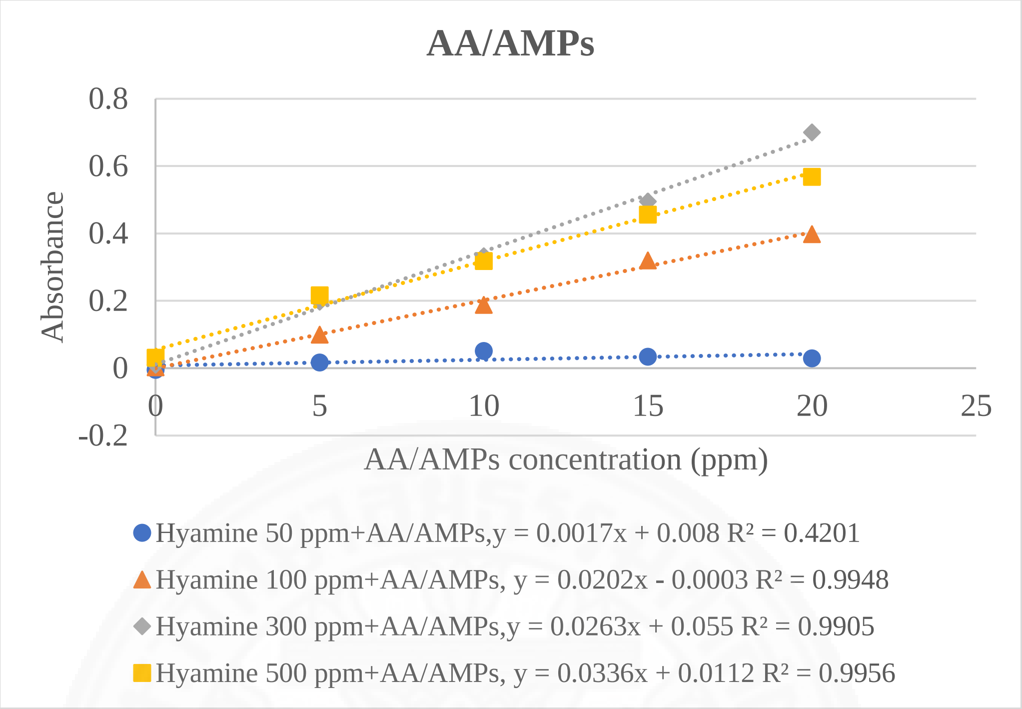


Figure 4.2 Absorbance result at 320 nm when using difference concentration of HI to form a complexation with AA/AMPs

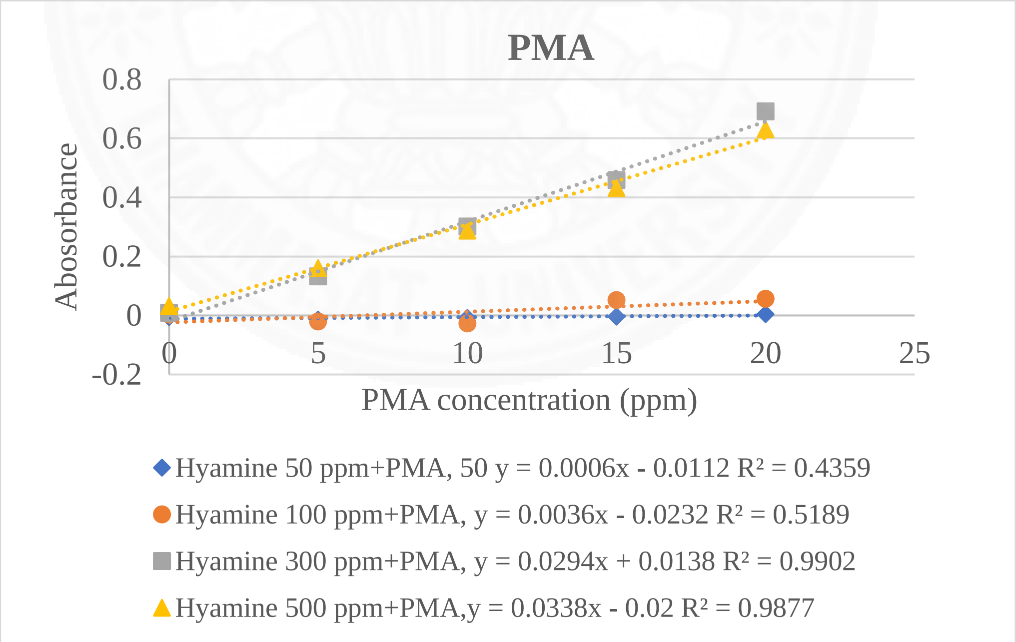
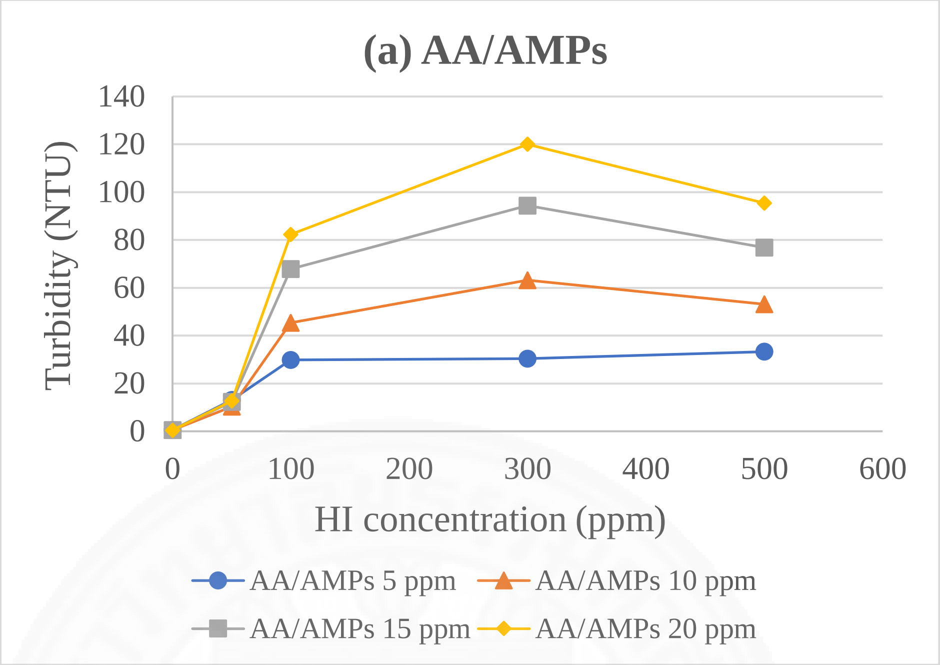


Figure 4.3 Absorbance result at 320 nm when using difference concentration of HI to form a complexation with PMA



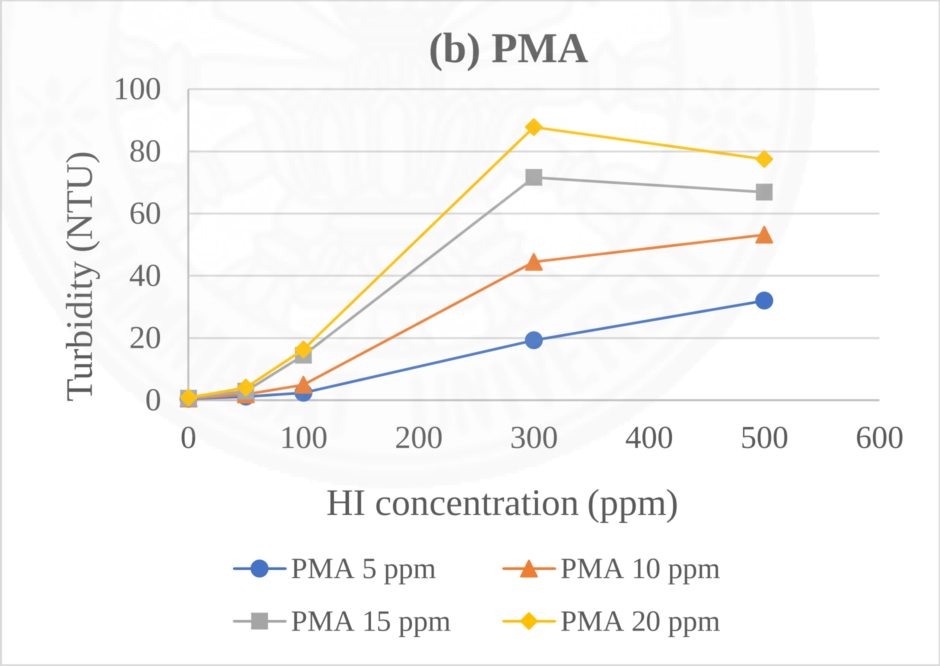


Figure 4.4 Turbidity of various concentrations of HI mixed with (a) AA/AMPs, (b) PMA

4.2.2.1 Distinguishing the two AS polymers using a single HI 100 ppm concentration

Based on the absorbance and turbidity response of the two polymers to the HI, it could be seen that at 100 ppm HI concentrations, the PMA at 20 ppm develops similar absorbance and turbidity to that of the AA/AMPs at 5 ppm.

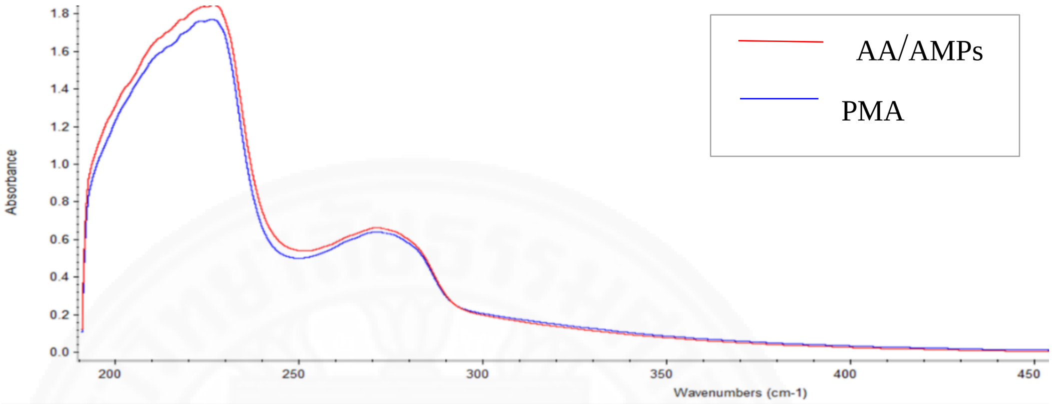


Figure 4.5 Comparison UV-Vis spectra result of 20 ppm of PMA and 5 ppm of AA/AMPs

The experiment should conduct with the specific wavelength and various reaction times in order to confirm the rate of these two types of AS when reacted with HI at 100 ppm. The absorbance was collected every minute until 40 minutes. Specific wavelength was selected at 320 nm. The graph was plot between reaction time and absorbance. As the result, the rate of PMA at 20 ppm had a similar trend to that of the AA/AMPs 5 ppm. Thus, this information is not enough for separating (Figure 4.6).

An attempt has been made to separate the two concentrations of polymers using HI at 100 ppm by taking the whole UV-Vis absorbance spectra and also by looking at the dynamics of complexation. However, it was not quite possible to distinguish PMA at 20 ppm from that of the AA/AMPs 5 ppm using just absorbance spectrum or time of complexation.

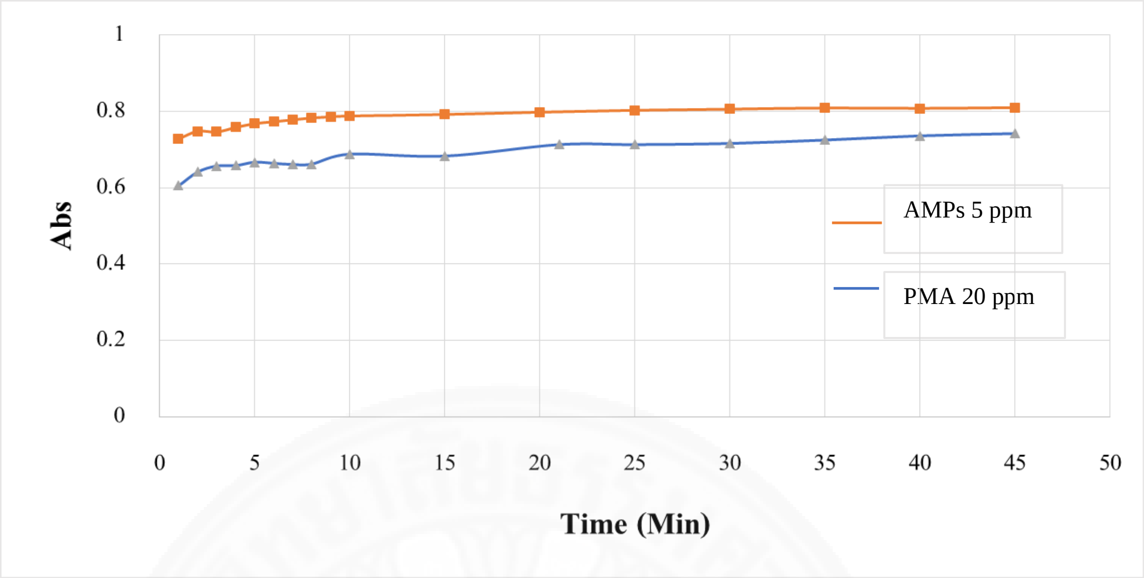


Figure 4.6 Comparison the rate of AA/AMPs 5 ppm and PMA 20 ppm (at 320 nm) to complexed with HI 100 ppm

To test if this was just coincidence, the effect of higher concentration of PMA to complex with HI 100 ppm was also tested with a larger PMA concentration 4 times of AA/AMPs concentration (PMA = 80 ppm, AA/AMPs = 20 ppm). The absorbance was then collected at 10 minutes for complexation.

The result from Figure 4.7 showed that increasing the PMA concentration more than 4 times of the AA/AMPs concentration, the spectrum is quite similar to that of the AA/AMPs at 20 ppm. Thus, this result can confirm that using only a single HI concentration e.g. at 100 ppm cannot separate the absorbance of the higher PMA concentration from that of the lower concentration of AA/AMPs. The technique should also need to use another concentration of HI for analysis or separation of the two polymer concentrations. Thus, HI at 100 ppm and 300 ppm were selected for AS concentration determination.

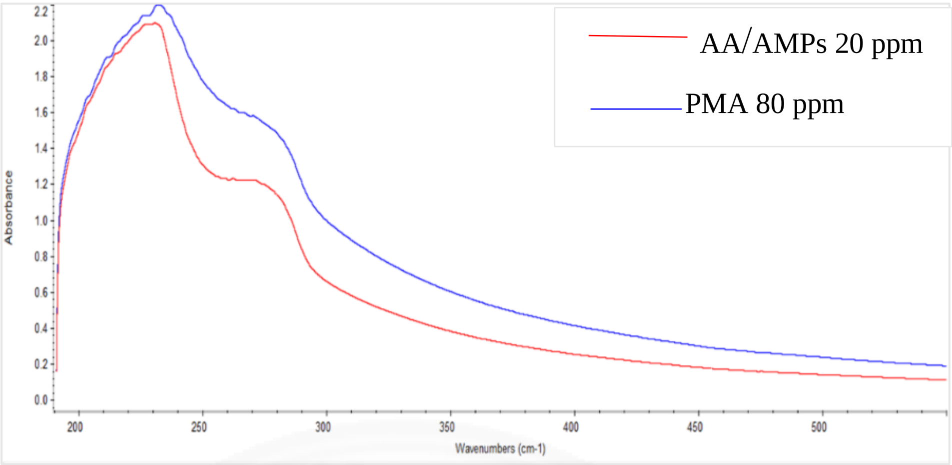


Figure 4.7 The effect of HI 100 ppm to higher concentration of PMA (80 ppm) compared to AA/AMPs 20 ppm

4.3 Characterizations of AS and HI

4.3.1 Effect of HI concentration at 20 ppm AS concentration

Various concentrations of HI were mixed with fixed amount of AS concentration (20 ppm of AA/AMPs or PMA) to investigate the effect HI concentration to an oppositely charged polymer. Zeta potential and turbidity were measured after 10 minutes reaction time.

4.3.1.1 Zeta potential

The result showed that increasing HI concentration explicitly promoted zeta potential change from negatively charged to positively charged of the complexation. Bared anti-scalant normally presented negatively charged due to their functional group in the backbone of polymer chain that contain both SO_3H and COOH for AA/AMPs. Only COOH played as a key functional group for PMA. Adding cationic surfactant resulted in the form of complexation.

Increasing HI concentration from 50 ppm to 200 ppm showed the negatively charged decreasing. The result was indicated that surfactant started to bind with polymer chain from a surfactant concentration at 50 ppm. AA/AMPs has two functional groups that can be protonated the negatively charges for the complexation, thus the negatively charged after complexed with small amount of oppositely charged surfactant remained higher than PMA complexed with surfactant. On the other hand, charge neutralization was occurred upon adding more surfactant to the system. At 300 ppm HI condition, charge of the complexation was almost equal to zero or neutralize value. Turbidity reached the maximum value as shown in Figure 4.8. The result was supported other works (Goddard, 1994; Goddard & Hannan, 1976; Goswami, Borreguero, Pincus, & Sumpter, 2015).They reported that, the maximum binding was occurred when the charge of particle equal to zero which mean polymer- surfactant binding was occurred completely (Goddard, 2002). Adding higher concentration of cationic surfactant resulted in an increasing of positively charged on the surface of particle. Further increasing HI concentration from 400 ppm to 700 ppm, charge upturn to positive completely which means the amount of surfactant excessed in the system. This result can be indicated that the second layer of surfactant molecules were formed at the surface of complexed particle.

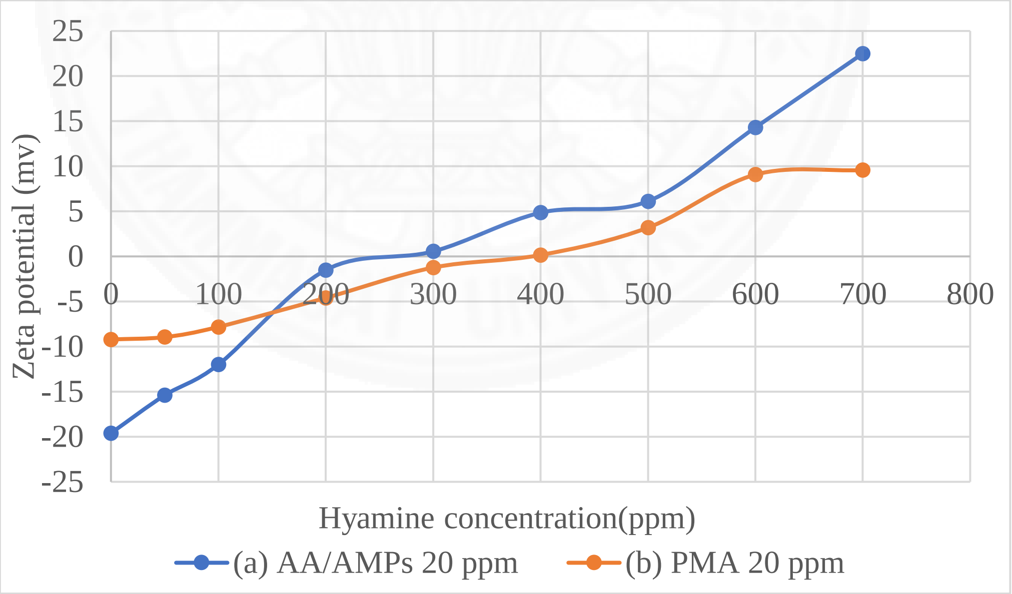


Figure 4.8 Zeta potential of various concentrations of HI mixed with; (a) AA/AMPs 20 ppm, (b) PMA 20 ppm

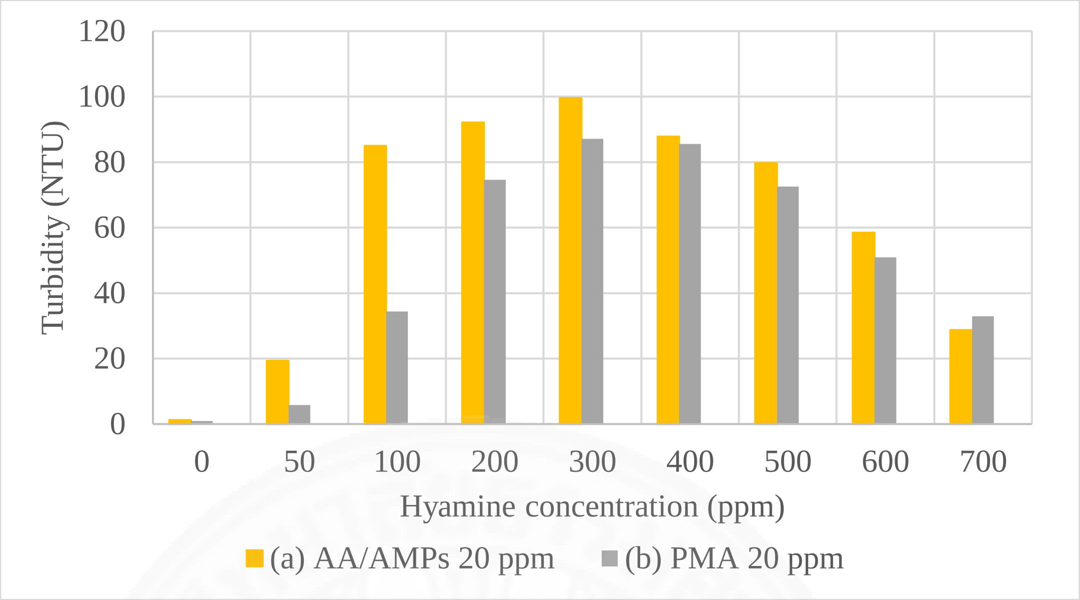


Figure 4.9 Turbidity of various concentrations of HI mixed with; (a) AA/AMPs 20 ppm, (b) PMA 20 ppm

Turbidity was measured to confirm the complexation between these two types of chemicals as showed in Figure 4.9. The result showed that turbidity was developed when increasing HI concentration from 50 ppm to 300 ppm. The maximum value was obtained at 300 ppm HI. The maximum turbidity were 99.5 NTU and 87.1 NTU for AA/AMPs and PMA, respectively. A drop in turbidity was then observed at 400 ppm to 700 ppm HI.

Particle size was also measured in this case, the result was showed in the table Appendix A, Table 14. The size average referred to quality report as indicated that the particle became too polydisperse and cannot detect via the measurement and hence the results from particle sizer could not be used for analysis.

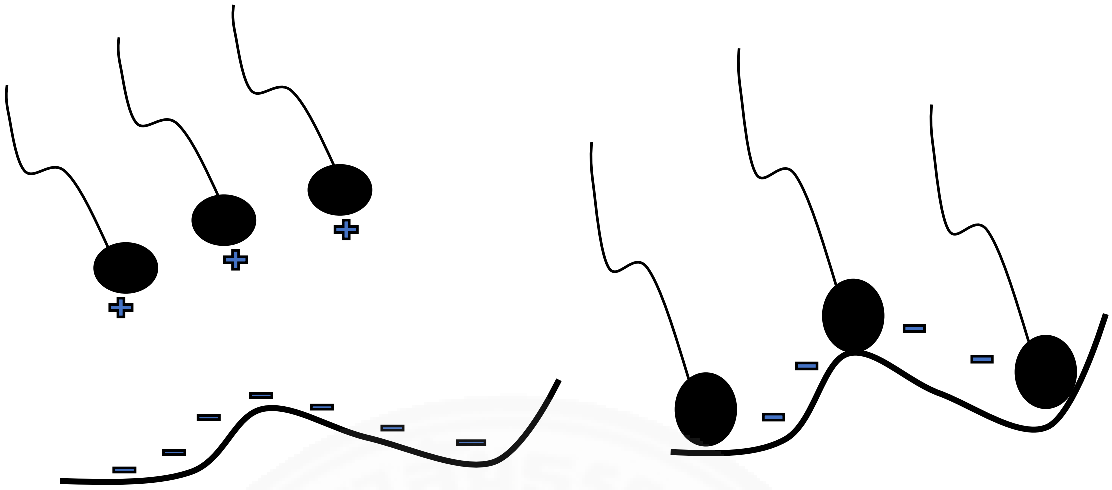


Figure 4.10 Electrostatic driving force between oppositely charge of AS polymer and surfactant

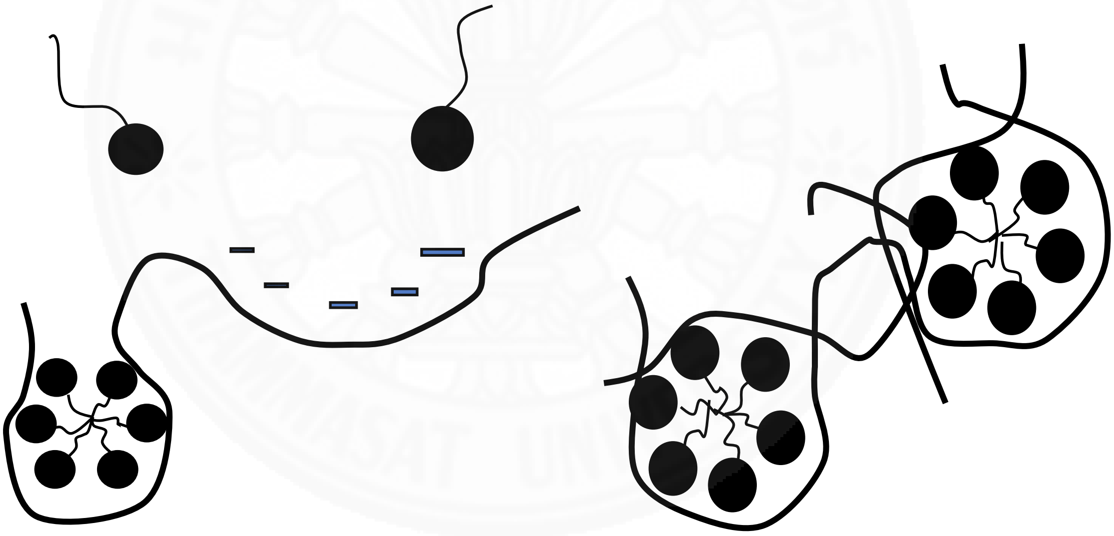


Figure 4.11 Hydrophobic driving force between aliphatic tail of surfactant

4.3.2 Effect of various concentrations of AS with 100 ppm and 300 ppm of HI

The effect of HI concentration to polymer-surfactant complexation from previous study can confirm that the maximum precipitation point occurred at 300 ppm of the surfactant. Zeta potential of this condition became nearly to zero (neutral) and turbidity led to maximum value for both AA/AMPs and PMA. Thus, the concentration of HI was then selected at 100 ppm and 300 ppm for AS concentration determination. Various concentrations of AS were prepared to study the effect of polymer concentration with HI.

4.3.2.1 Zeta potential

Polymer anti-scalant complexed with surfactant results in formation of a larger particle which can be easily detected as an increase in turbidity and absorbance. To gain further understanding of this complexed particle formation, zeta potential and size of the particles are studied in term of a zeta potential and particle size.

Zeta potential is the one technique that can be used to assess charges of the particle complex formed.

Table 4.2 Zeta potential of stock solution

Sample	Zata potential (mV)
Make up water	-10.4
AA/AMPs 1,000 ppm in DI water	-16.9
PMA 1,000 ppm in DI water	-7.71
HI 1,000 ppm in DI water	34.2

Table 4.2 showed the amount of charges from stock solution of anti-scalant are -16.9 mV and -7.71 mV for AA/AMPs and PMA, respectively. Anti-scalant charges

depended on functional group that contained in the polymer chain. AA/AMPs has two types of functional groups that can be protonated e.g. SO_3H and COOH. Only COOH played as a key functional group of PMA for complexation. As the result, the amount of negatively charged from AA/AMPs was higher than PMA. Make up water also seem to contain some the negatively charged particles in the system. Positively charge only showed with HI that was a cationic surfactant.

The charge profile of polymer-surfactant complexation at difference concentration of the polymer was shown in Figure 4.12. The evaluation of zeta potential as a function of HI concentration (100 ppm and 300 ppm) with difference concentration of polymers (5 ppm, 10 ppm, 15 ppm and 20 ppm) showed that zeta potential of using HI concentration from 100 ppm to 300 ppm was increased due to increase positively charged of the surfactant in the system.

At 100 ppm HI, using 5 ppm of AS had a less net negatively charged of the complexed particles than using higher AS concentration. It can be indicated that, the small amount of negatively charged AS chains when using lower concentration of AS presented in the solution. Consequently, the chains were fulfilled with HI molecules and some of HI was the free molecule form due to the AS was insufficient in the system. As the result, the complexed particles presented less amount of negatively charge on surface.

Increasing the AS concentration led to have more amount of negatively charged AS chains bonded with HI. Many chains presented in the system, results in the competitive of binding with HI among AS chains. As the result, small amount of HI molecules can be bound with each chain of AS. But it should be noted that, there are many chains of AS in the solution which means the system has the small amount of binding AS-HI in any area of the solution. Thus, the small AS-HI binding can be bound together to form a larger particles aggregation. The higher net negatively charge was found when using higher concentration of AS.

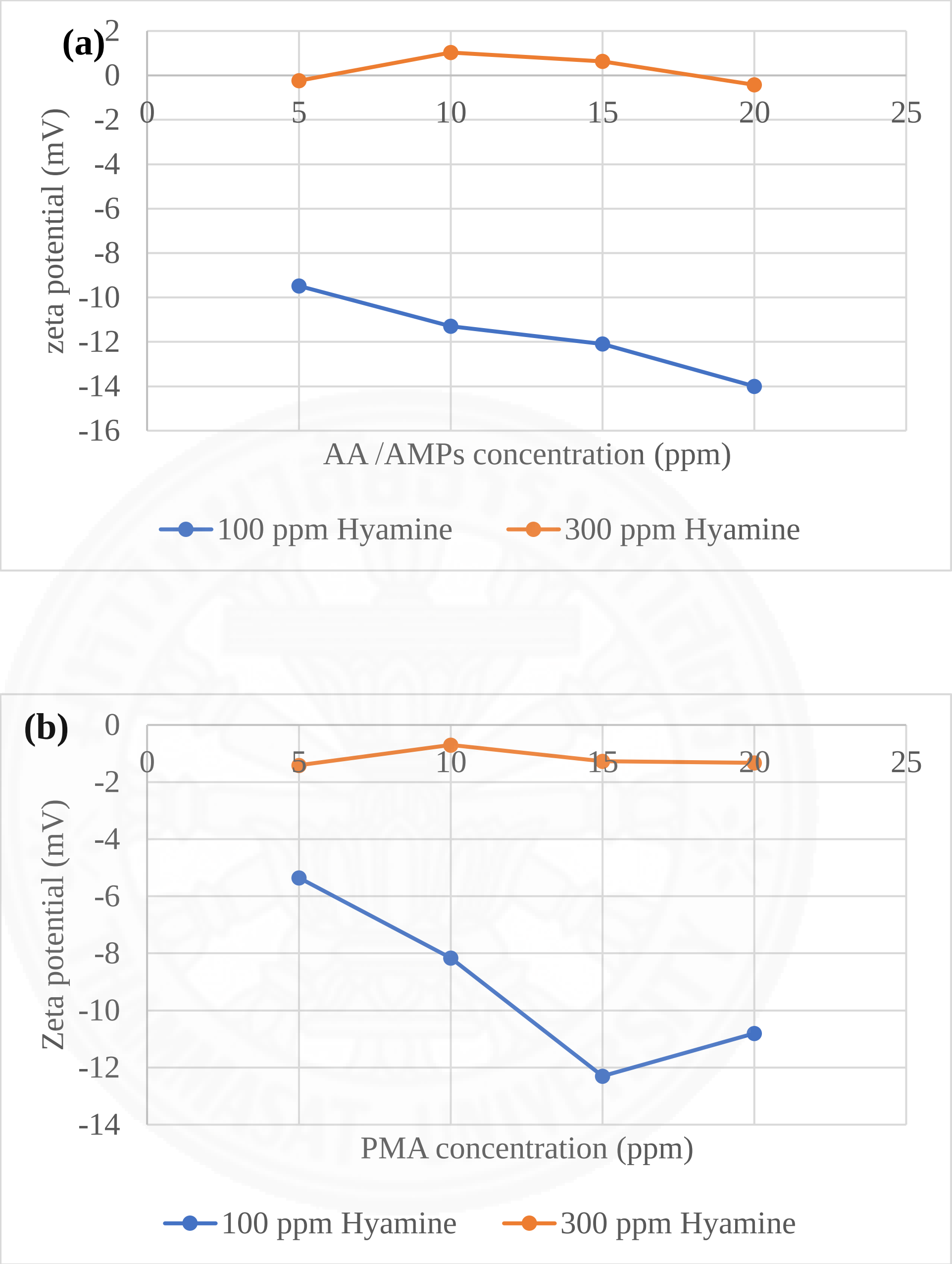


Figure 4.12 The evaluation of zeta potential as a function of surfactant concentration (100 ppm and 300 ppm) with difference concentration of AS; (a) AA/AMPs, (b) PMA

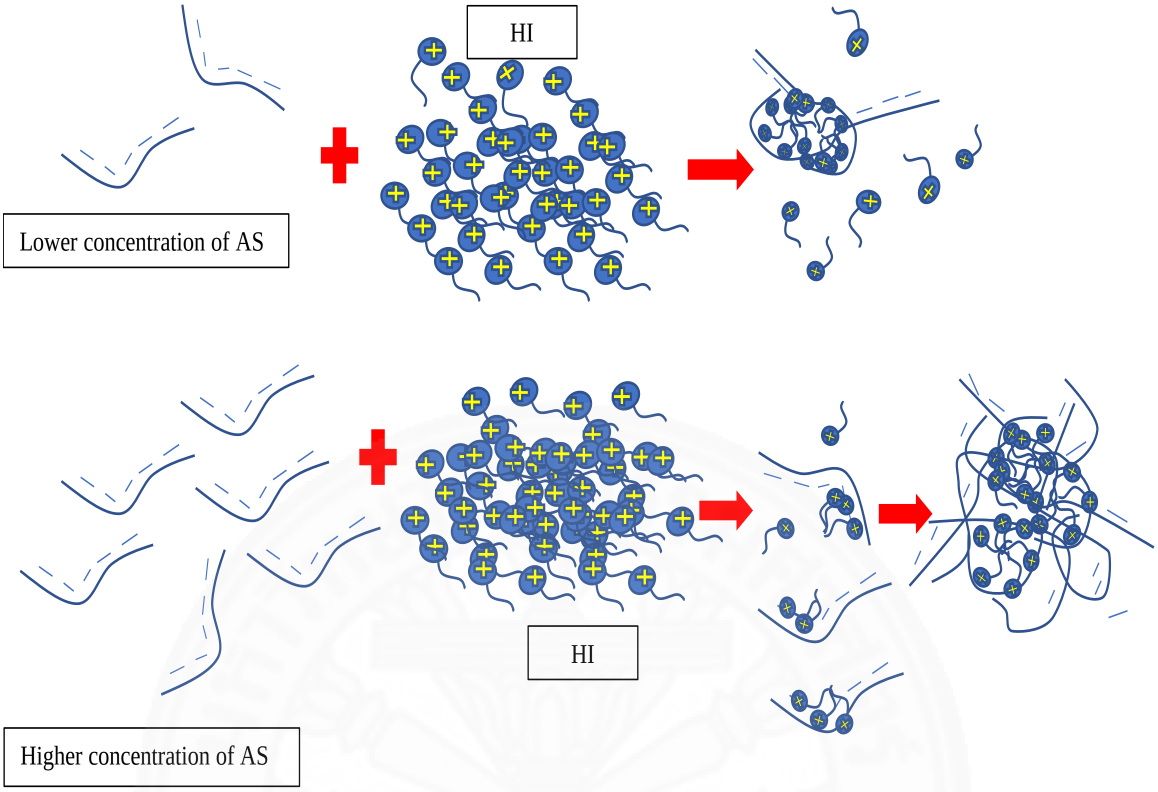


Figure 4.13 Schematic represented various concentrations of AS formed the complexed particles with HI

4.3.1.2 Turbidity and Particle size

The bared polymer was indicated to extend in the solution due to an electrostatic repulsion between the same charges along with the chain (Liu, 2015). The coiling in polymer chain can occur when increasing surfactant concentration in the system to complex with the polymer chain.

. At 100 ppm HI concentration, turbidity developed as linear correlation with a function of AA/AMPs concentration as shown in Figure 4.14 (a). Particle size result from Figure 4.16 showed that the particle size of AA/AMPs-HI has a larger particle size when increasing the AA/AMPs concentration from 5 ppm to 15 ppm complexed with 100 ppm of the surfactant. The electrostatic interaction was increased due to an increasing in the polymer concentration, which means more negatively charged can complex with the molecule of oppositely charged surfactant in the system. The result showed that the higher PDI was indicated that the particle became more larger and polydisperse. At 15 ppm of AA/AMPs, the quality report was not good probably due to the particles became too polydisperse and cannot detect via the measurement. Further increased the AA/AMPs concentration to 20 ppm, the particle size was observed not to larger but became smaller in particle size. A quality report showed a good result again as same as at the lower AA/AMPs concentration (5 ppm and 10 ppm).

In case of PMA, turbidity result was observed not to change significantly when complexed with surfactant at 100 ppm as shown in Figure 4.14 (b). The particle size increasing was quite similar to that of turbidity as shown in Figure 4.17. This can be discussed in term of the amount of charge along with the chain of polymer (Tseng, 2018). AA/AMPs is the macromolecule co-polymer that contained a higher negatively charge more than PMA, which means the number of charged groups are more available for electrostatic interaction with molecule of the surfactant. The critical aggregation concentration (CAC) of higher charged groups of AA/AMPs is lower than PMA. Thus, AA/AMPs can be bound with the surfactant even in the low concentration (5 ppm) and trended to increase in particle size when increasing the AA/AMPs concentration to complex with 100 ppm of HI. For PMA, higher HI concentration needs to add in the system for binding with the small molecule of PMA by electrostatic interaction. Then, the particle becomes the bigger size by hydrophobic interaction of HI.

The result was supported with the studied of Allisan, Wimberly and Ely (1987) who developed the technique for determination of polyacrelamide and other negatively charged polymers by using HI (cationic surfactant) as a complexing agent. Turbidity was measured the complexed particles. The sensitivity of technique was test with various types of polymer. They reported that the detection limit of polvacrylic-vinyl sulfonic acid copolymer can be dropped down to less than 1 ppm. On the other hand, polymaleic acid only had the detection limit equal to 1 ppm. The sensitivity of polvacrylic-vinyl sulfonic acid copolymer was higher than polymaleic acid. Hydrolysis content was discussed to have an effect to the sensitivity of the technique (J.D. Atlison, 1987).

When using higher concentration of HI reached to 300 ppm, it can be indicated that both electrostatic and hydrophobic interaction were introduced to the AS-HI system. Turbidity result was increased with increasing surfactant concentration from 100 ppm to 300 ppm significantly as shown in Figure 4.15 (a), (b). The bigger particle size indicated that the random-coil size configuration was formed with increasing HI concentration. On the other hands, the bigger particle size cannot be measured via the zeta sizer machine. The quality report referred about too polydisperse of particle in the solution and hence the results from particle sizer could not be used for analysis. However, the result was shown in the table 13, appendix A.2

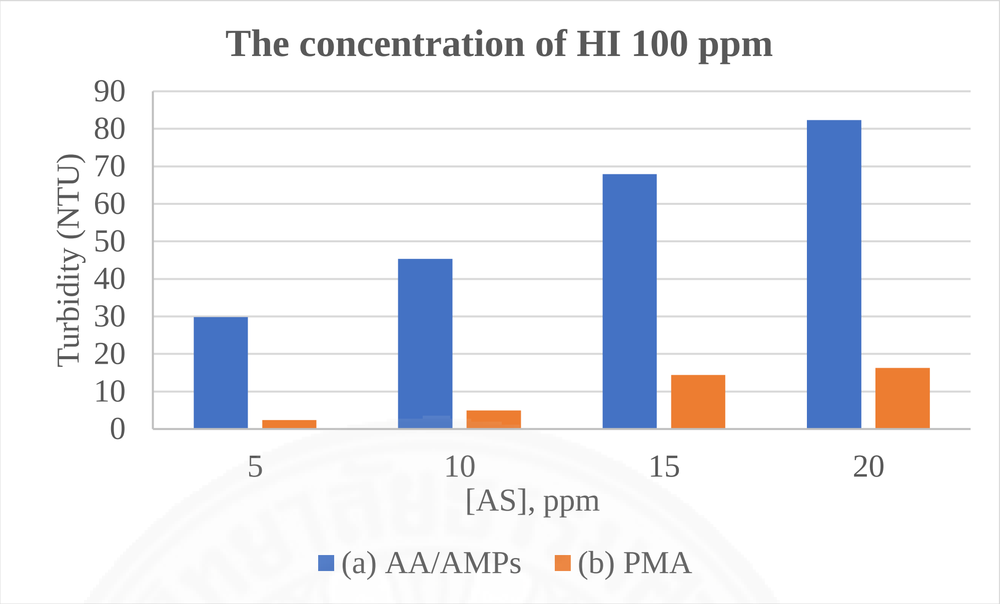


Figure 4.14 Turbidity of the anti-scalant complexed with HI at 100 ppm

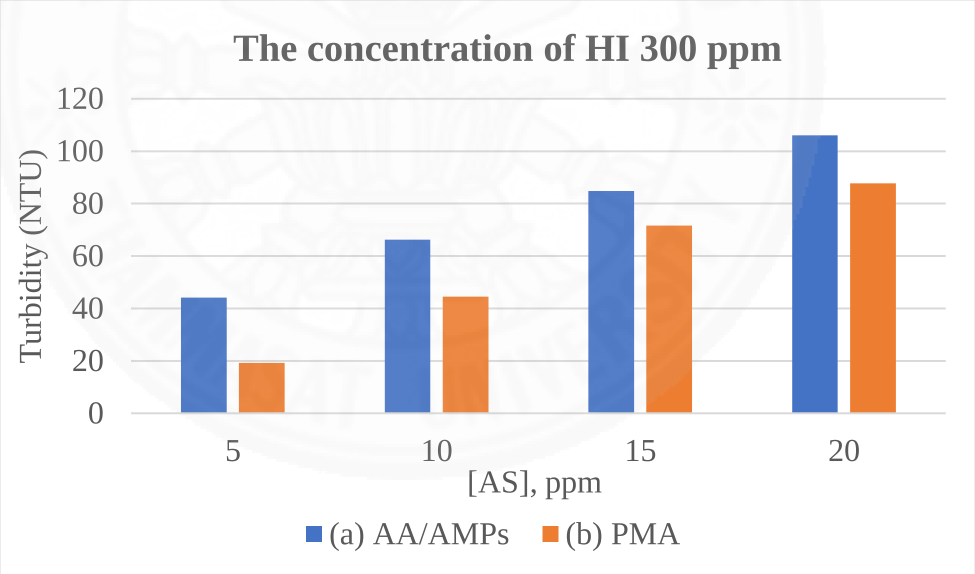


Figure 4.15 Turbidity of the anti-scalant complexed with HI at 300 ppm

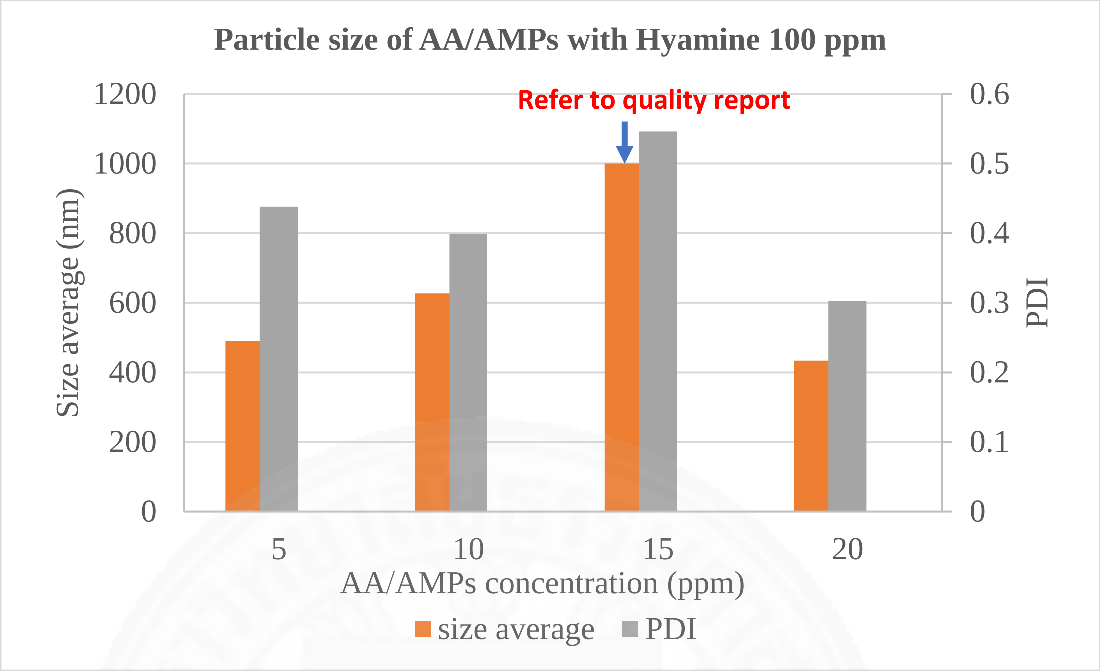


Figure 4.16 The particle size and PDI of various concentrations of AA/AMPs mixed with HI 100 ppm

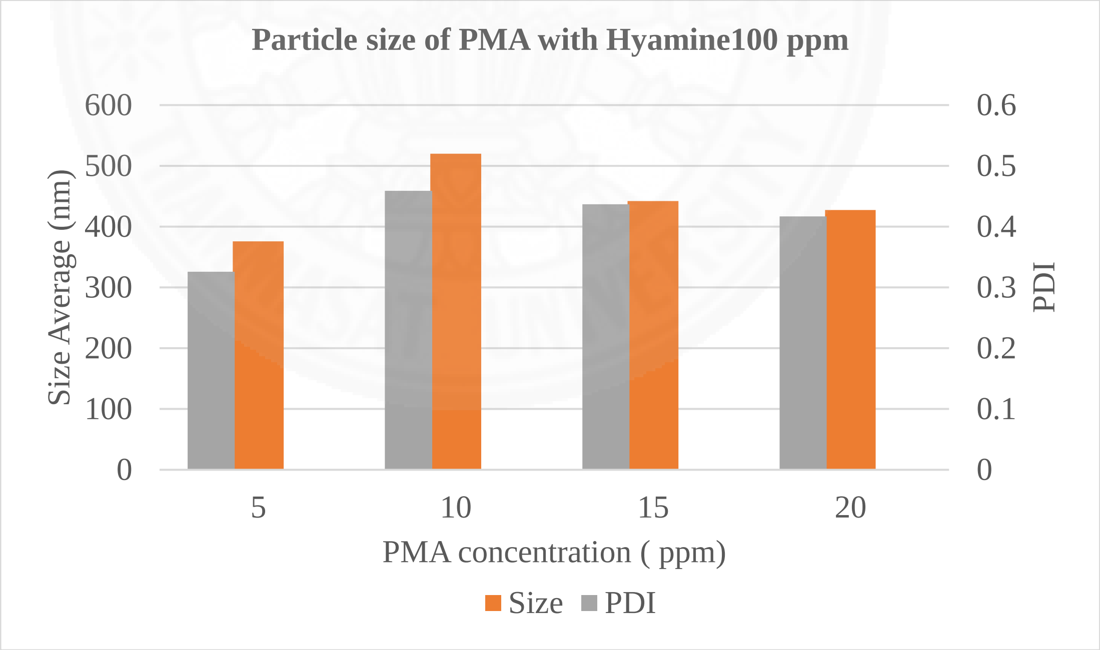


Figure 4.17 The particle size of various concentrations of various concentration of PMA mixed with HI 100 ppm

4.4 Study the effect of calcium ion to the development technique

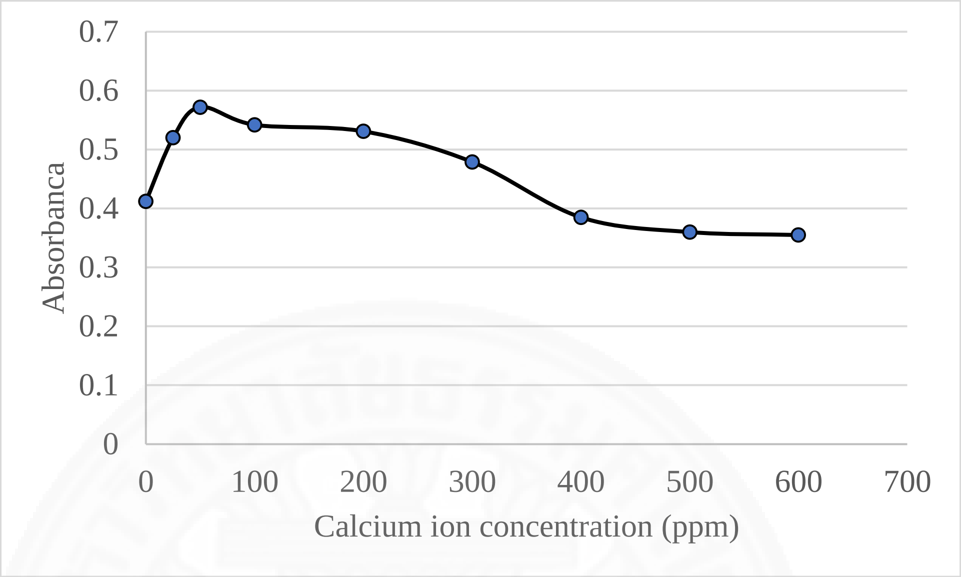


Figure 4.18 The effect of calcium ion to absorbance of complexation

The relation of absorbance and Ca^{2+}increasing is revealed in Figure 4.18. Firstly, the absorbance of AS-HI increased when contained Ca^{2+} 25 ppm to 100 ppm in the water sample. The absorbance increasing at the first phase can probably discuss in term of ionic strength aids the small particles to come closer together. On the other hands, further increasing salt concentration (200 ppm to 600 ppm) can lead to screen the available charge on the polymer chain which means some of polymer react with the Ca^{2+} and less number forms complex with the surfactant result in absorbance decreasing (Khan, 2018).

The result showed that calcium ion affected the development technique in term of absorbance decreasing when increased calcium ion concentration from 200 ppm to 600 ppm Ca^{2+}.

As the result, the specific coefficient of specific water sample mixed with HI at 100 ppm and 300 ppm was suggested to calculate for analysis, due to the water sample has the variation of Ca^{2+}. The technique aims to detect the ‘free polymer’ which available complex with HI.

4.5 Test of interferences

4.5.1 Effect of 2-Phosphonobutane-1,2,4-tricarboxylic acid (PBTC) to the development technique

PBTC was tested with 100 ppm HI as a pure component and in the mixture with AA/AMPs and PMA. The result showed that pure PBTC did not show the effect in term of turbidity and absorbance increasing when increased concentration.

Table 4.3 Effect of pure PBTC and mixture component of PBTC to turbidity when complexed with HI 100 ppm

PBTC concentration (ppm)	Turbidity (NTU)	
	Pure PBTC	PBTC mixed with AA/AMPs and PMA 5 ppm
0	3.57	38.9
5	4.17	35.3
10	5.65	39
20	4.25	39.6

The result shows in Table 4.3, turbidity is increased around 35 NTU that had the same result of the complexation between pure component of AA/AMPs at 5 ppm (Turbidity = 29.89 NTU) and PMA 5 ppm (turbidity 2.37 NTU) mixed with HI at 100 ppm. It can be summarized that PBTC does not have a synergistic effect in term of turbidity generation with AA/AMPs and PMA when the solution was mixed with HI. Turbidity in this case was obtained from AA/AMPs and PMA. The result showed that we can use this technique for AA/AMPs and PMA concentration analysis when it is in the system that also added PBTC in the water-cooling system.

4.5.2 Effect of sulfate to the development technique

Figure 4.19 showed that SO_4^{2-} affected the AS-HI system at 100 ppm and 300 ppm HI concentration when mixed with AA/AMPs 20 ppm dissolved in the synthetic water ([Ca^{2+}] 100 ppm in DI) in term of turbidity deceasing. On the contrary, using HI at 500 ppm can have the synergistic effect in term of turbidity generation at 125 ppm to 1,000 ppm SO_4^{2-} . Further increased SO_4^{2-} results in turbidity decreasing quite similar to that of the 100 ppm and 300 ppm HI. This result can discuss in term of charge compensation.

HI has a positively charge particle which are available to bind with both negatively charge of AS and SO_4^{2-}. At 100 ppm and 300 ppm HI, the surfactant molecules were enough to bind with AS and generate the turbidity at 10 minutes reaction time. Adding SO_4^{2-} 125 ppm to 500 ppm was not affect to the AS-HI system. Further increased SO_4^{2-} from 625 ppm to 1,500 ppm means HI molecules can be bind with the excess SO_4^{2-} instead to bind with AS. Consequently, turbidity result was decreased because the available HI is less to form the complexed particles with AS.

At 500 ppm HI, it should be noted that the excess molecules of surfactant presented in the system. This HI concentration can redissolve the complexed particles due to the excess molecules of the surfactant can form a second layer on the surface of neutral particles from the previous study. Adding SO_4^{2-} means increasing negatively charge to the system, that can interact with the excess positively charged molecules of the surfactant. Thus, less second layer can form on the surface of neutral complexed particles. The turbidity was then increased with increasing SO_4^{2-} from 125 ppm to 1,000 ppm. Further increased SO_4^{2-} from 1,500 ppm to 2,500 ppm, turbidity was decreased quite similar to that of the 100 ppm and 300 ppm HI concentration.

In the actual cooling system operation, the concentration of sulfate was controlled to not over 200 ppm for SO_4^{2-}. Thus, sulfate in the actual cooling system does not affect to the development technique.

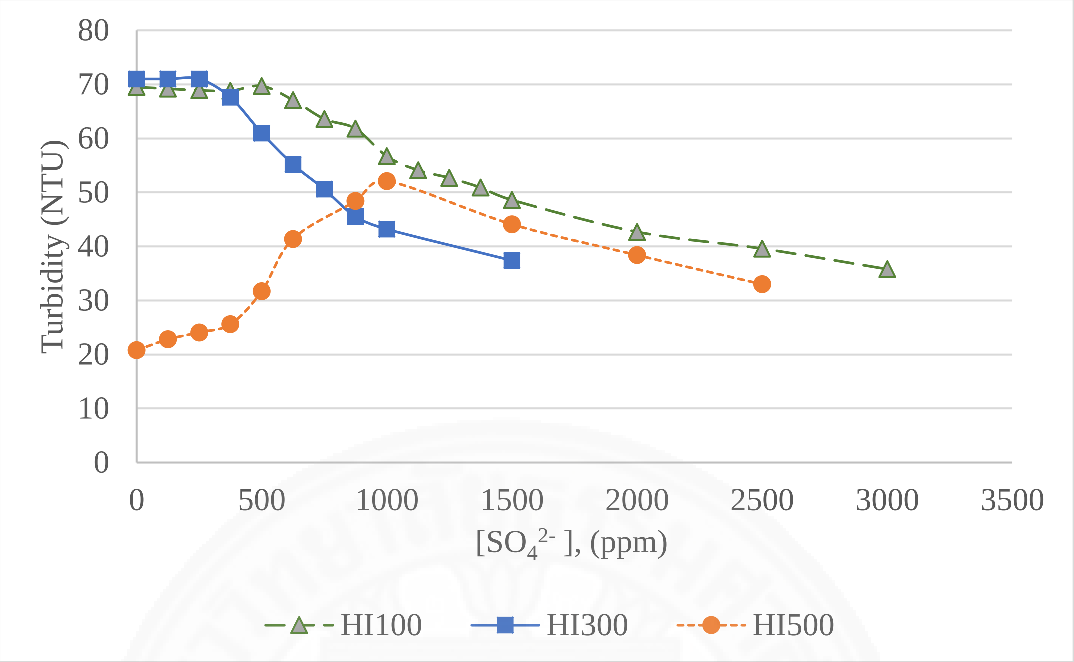


Figure 4.19 Effect of sulfate to the development technique

4.6 AS concentration determination

Figure 4.20 and 4.21 revealed that AA/AMPs gave the higher complexation rate with 100 ppm HI more than PMA significantly. Increasing surfactant concentration to 300 ppm, the complexation rate of AA/AMPs and PMA gave almost the same rate for absorbance increasing.

In order to test the ability of the current method for prediction, the water from actual cooling system was required to measure the AS concentration. This cooling water from an electrical power plant contains certain amount of AA/AMPs and PMA, but the precise value was not known as the system has been continuously operating and the water sample collected mid-cycle of the operation. To test the ability of the technique to predict value of AA/AMPs or PMA in the actual water sample, the water sample was spiked with series of known concentrations of AA/AMPs or PMA, reacted with HI 100 ppm, 300 ppm and the absorbance was measured at 320 nm. The change in the AA/AMPs or PMA concentrations obtained from the model was then obtained.

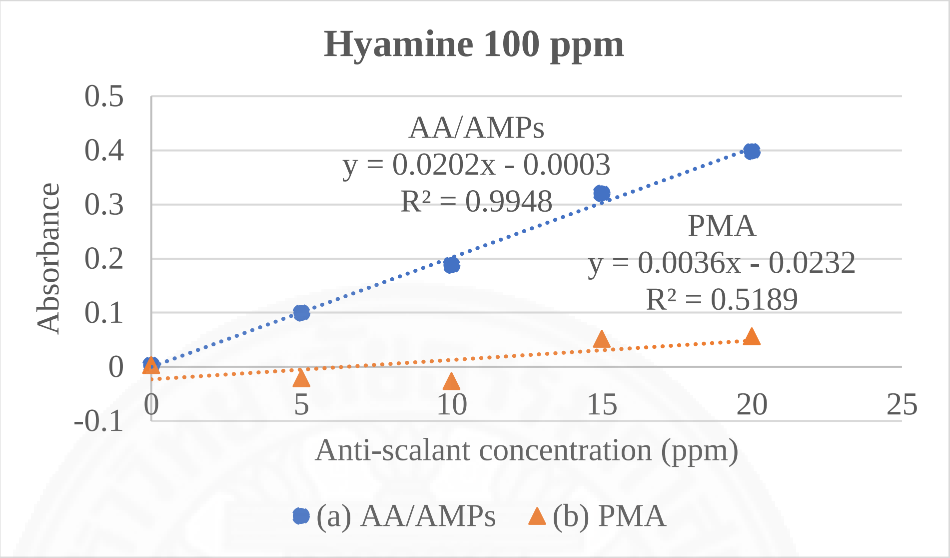


Figure 4.20 Absorbance result of HI 100 ppm with various AS concentrations of;

(a) AA/AMPs and (b) PMA

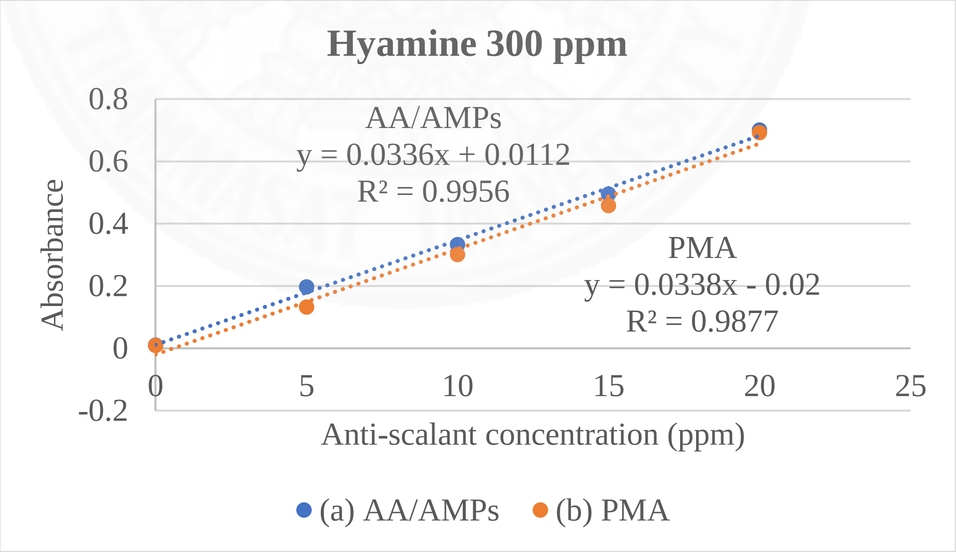


Figure 4.21 Absorbance result of HI 300 ppm with various AS concentrations of;

(a) AA/AMPs and (b) PMA

Coefficient was calculated at the first. The unknown actual cooling water sample (A) was reacted with HI 100 ppm and 300 ppm. Absorbance was collected after 10 minutes reaction time. AA/AMPs 20 ppm was then spiked in the unknown water sample to react with HI at 100 ppm and 300 ppm. In case of PMA, only 300 ppm HI will be used for coefficient calculation. The absorbance and coefficient result were shown in Table 4.4.

Coefficient was then calculated as follow;

- Coefficient of AA/AMPs at 100 ppm HI;

$$Coeff.AA/AMPs_{100\ HI} = \frac{(0.395 - 0.062)}{20} = 0.023$$

- Coefficient of AA/AMPs at 300 ppm HI;

$$Coeff.AA/AMPs_{300\ HI} = \frac{(0.797 - 0.181)}{20} = 0.041$$

- Coefficient of PMA at 300 ppm HI;

$$Coeff.PMA_{300\ HI} = \frac{(0.797 - 0.181)}{20} = 0.024$$

Table 4.4 The absorbance and coefficient result of the unknown actual cooling water (A)

Sample	Absorbance		Coefficient	
	HI 100 ppm	HI 300 ppm	HI 100 ppm	HI 300 ppm
Actual cooling water (A)	0.062	0.181	-	-
Spiked AA/AMPs 20 ppm in actual cooling water (A)	0.395	0.797	0.023	0.041
Spiked PMA 20 ppm in actual cooling water (A)	-	0.542	-	0.024

Concentration analysis of AA/AMPs or PMA can be calculated from the coefficient and absorbance of HI at 100 ppm and 300 ppm using the equation (3.8) and (3.9) for AA/AMPs and PMA, respectively.

$$S1 = Y100/a1$$

$$S2 = Y300_{PMA}/b1$$

Table 4.5 shows the calculated concentration result of the unknown actual cooling water sample (A) that was spiked with AA/AMPs and PMA 5 ppm, 10 ppm and 15 ppm. The concentration of AA/AMPs obtained from the equation was then 7.28 ppm, 12.45 ppm and 17.80 ppm, respectively. The concentration of PMA as calculated from the model was to be 7.70 ppm, 11.35 ppm and 14.90 ppm, respectively. It can be seen from the plot that the predicted increase in AA/AMPs or PMA concentration follows quite well as the experimental increase (spike) in the AA/AMPs and PMA. The linear relation between the added amount and the measured amount was obtained with the slope of 1.00 and 0.80 for AA/ AMPs and PMA, respectively. It indicates a good correspondence between the experimentally added AS amount and the measured response of the model for AA/AMPs. But PMA, the calculated concentration value was under estimation from the experimentally added AS concentration slightly. The correlation between the calculated values and the experimental values has the R^2 value of 0.9984 and 0.9935 for AA/AMPs and PMA as shown in Figure 4.22 (a) and (b), respectively. Extrapolating the graph to the zero concentration yields the value of 2.55 ppm and 3.15 ppm, which is the predicted value of the active AA/AMPs and PMA in this cooling water sample (A), respectively. The accuracy of this value is not known as currently there is no easy way to measure the amount of the AS that remained in the cooling water system, however, given the high linear response of the spiked concentration with the slope of almost one, the value should be quite close to the actual value of AA/AMPs or PMA in cooling system.

Table 4.5 The spiked concentration determination analysis of the unknown actual cooling water (A)

Sample	Spiked AS concentration (ppm)	[AS] calculation, (ppm)	
		AA/AMPs	PMA
Actual cooling water (A)	0	2.55	3.15
Spiked AA/AMPs in actual cooling water (A)	5	7.28	6.41
	10	12.45	6.07
	15	17.80	2.76
Spiked PMA In actual cooling water (A)	5	3.61	7.68
	10	5.90	11.35
	15	4.47	14.90

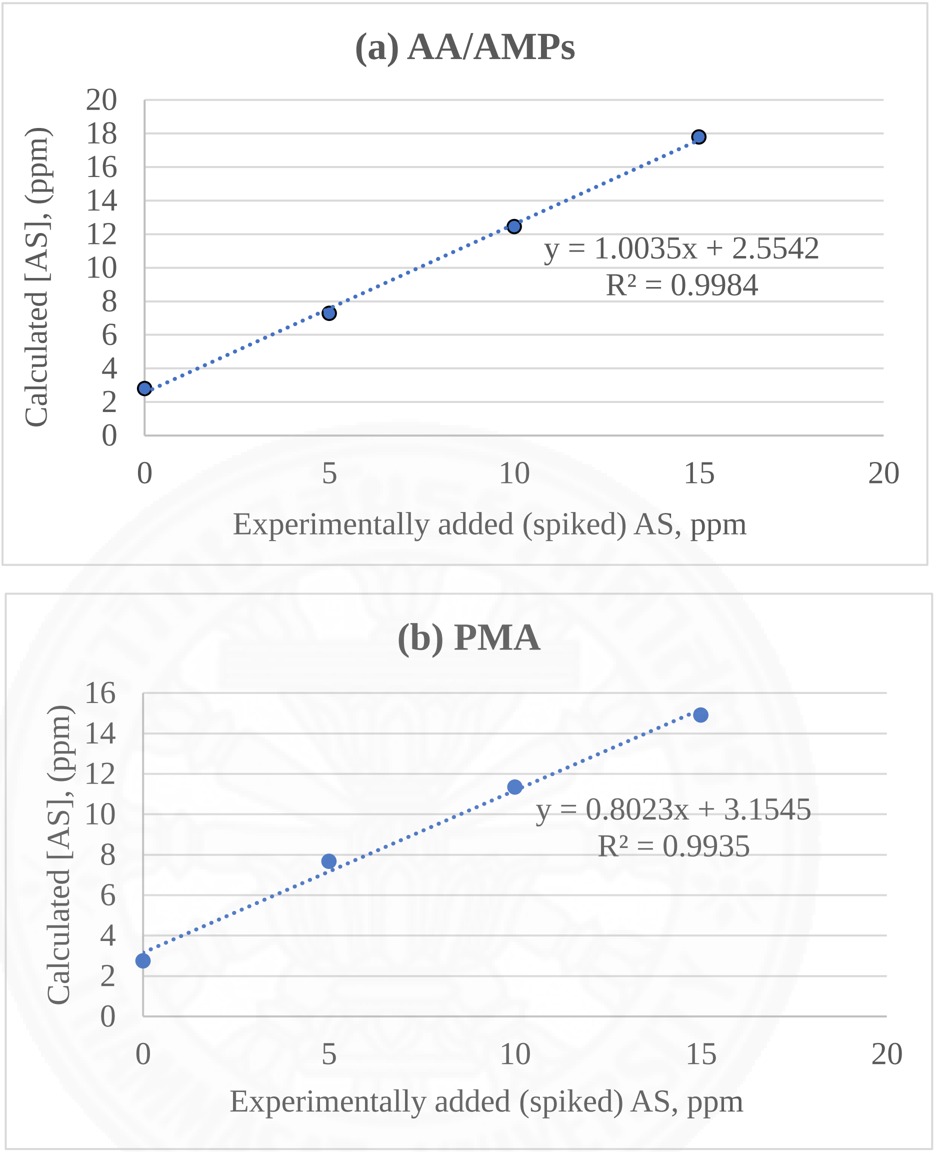


Figure 4.22 The correlation between the calculated AS concentration and the experimentally added AS concentration of the cooling water sample (A) using HI 100 ppm and 300 ppm; (a) AA/AMPs and (b) PMA

Another unknown actual cooling water sample (B) was also tested to determine the AS concentration by using spiked method with another concentration of HI at 150 ppm and 300 ppm to find the coefficient of AA/AMPs. Only 300 ppm of HI concentration was used for PMA coefficient calculation. Absorbance was collected after 10 minutes reaction time. The result of absorbance and coefficient was shown in table 4.6.

Table 4.6 The absorbance and coefficient result of the unknown actual cooling water (B)

Sample	Absorbance		Coefficient	
	HI 150 ppm	HI300 ppm	HI 150 ppm	HI 300 ppm
Actual cooling water (B)	0.277	0.479	-	-
Spiked AA/AMPs 20 ppm in actual cooling water (B)	0.594	0.835	0.016	0.018
Spiked PMA 20 ppm in actual cooling water (B)	-	0.586	-	0.005

Concentration analysis of AA/AMPs or PMA in the actual cooling water (B) can be calculated from the coefficient and absorbance of HI at 150 ppm and 300 ppm. The calculated AS concentration of the unknown actual cooling water (B) was reported in table 4.7.

Table 4.7 The spiked concentration determination analysis of the unknown actual cooling water sample (B)

Sample	Spiked concentration (ppm)	[AS] calculation, (ppm)	
		AA/AMPs	PMA
Actual cooling water (B)	0	17.42	31.57
Spiked AA/AMPs in actual cooling water (B)	5	22.58	29.74
	10	27.17	32.78
	15	33.02	33.88
Spiked PMA In actual cooling water (B)	5	15.09	43.80
	10	15.66	43.41
	15	15.72	50.49

The result from the experimentally added AS concentration and calculated AS concentration from the model of cooling water sample (B) was then plotted to see the relation of these values as shown in figure 4.23 (a), (b). It can be seen from the plot that the predicted increase in AA/AMPs or PMA concentration follows quite well as the experimental increase (spike) in the AA/AMPs and PMA. The linear relation between the added amount and the measured amount was obtained with the slope of 1.03 and 1.13 for AA/AMPs and PMA, respectively. Extrapolating the graph to the zero concentration yields the value of 17.34 ppm and 33.86 ppm, which is the predicted value of the active AA/AMPs and PMA in this cooling water sample (B).

The operated condition for cooling system was 20 ppm for both AA/AMPs and PMA. Compared the predicted AS concentration value from the spiked method with the calculated AS concentration value from the coefficient calculation (AA/AMPs 17.42 ppm and PMA 31.57 ppm), the result showed that the operator used the overdose of PMA for cooling system operation.

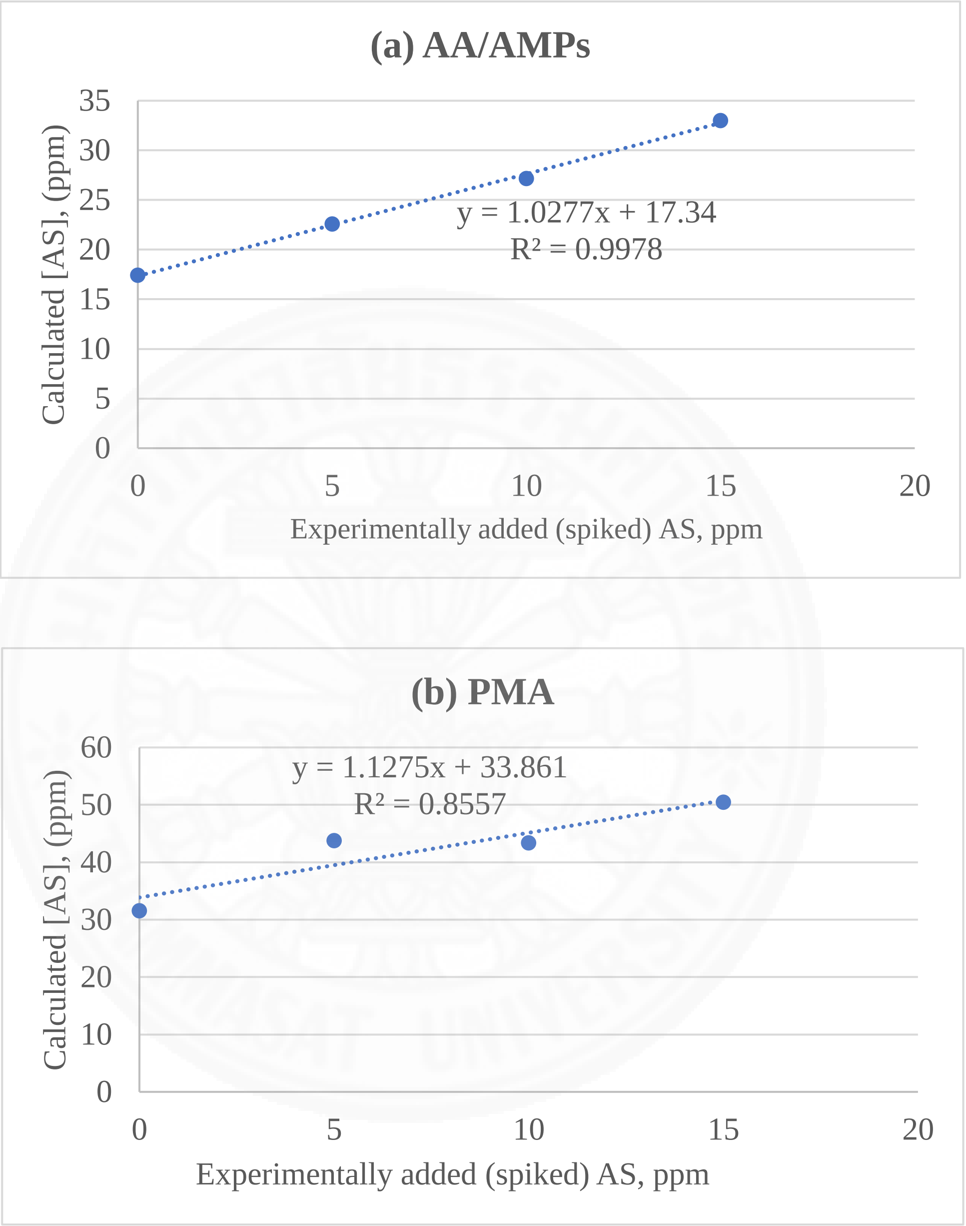


Figure 4.23 The correlation between the calculated AS concentration and the experimentally added AS concentration of the cooling water sample (B) using HI 150 and 300 ppm; (a) AA/AMPs and (b) PMA

AS concentration determination in make-up water

From previous study, AS concentration in actual cooling water sample was calculated from spiked method. The high linear response of the spiked concentration with the slope of almost one was assumed that the value should be quite close to the actual value of AA/AMPs or PMA in cooling system. However, the accuracy of this value is not known.

In order to test the ability of the method clearly, known amount of AS in water sample was used for testing.

Make-up water is the water from the natural river that is used for cooling operation to maintain salinity and conductivity in the cooling system. The water is considered as free AS water sample. The method was demonstrated by using spiked method with AS 15 ppm into the make-up water as same as in the actual cooling water. AA/AMPs coefficient was then calculated from HI 100 ppm and 300 ppm. Only HI 300 ppm was used for coefficient of PMA calculation. The result was shown in Table 4.8.

Table 4.8 The absorbance and coefficient result of the make-up water

Sample	Absorbance		Coefficient	
	HI 100 ppm	HI 300 ppm	HI 100 ppm	HI 300 ppm
Make-up water	0.003	0.01	-	-
Spiked AA/AMPs 15 ppm in make-up water	0.320	0.495	0.021	0.032
Spiked PMA 15 ppm in make-up water	-	0.458	-	0.030

In order to test the ability of the current method for prediction, both AA/AMPs and PMA were spiked in the pure make-up water as the single and mixture component. The sample was then reacted with HI 100 ppm and 300 ppm. Absorbance was collected after 10 minutes reaction time at 320 nm.

Concentration analysis of AA/AMPs or PMA can be calculated from the coefficient and absorbance using HI at 100 ppm and 300 ppm for complexation. The calculation result was shown in Table 4.9.

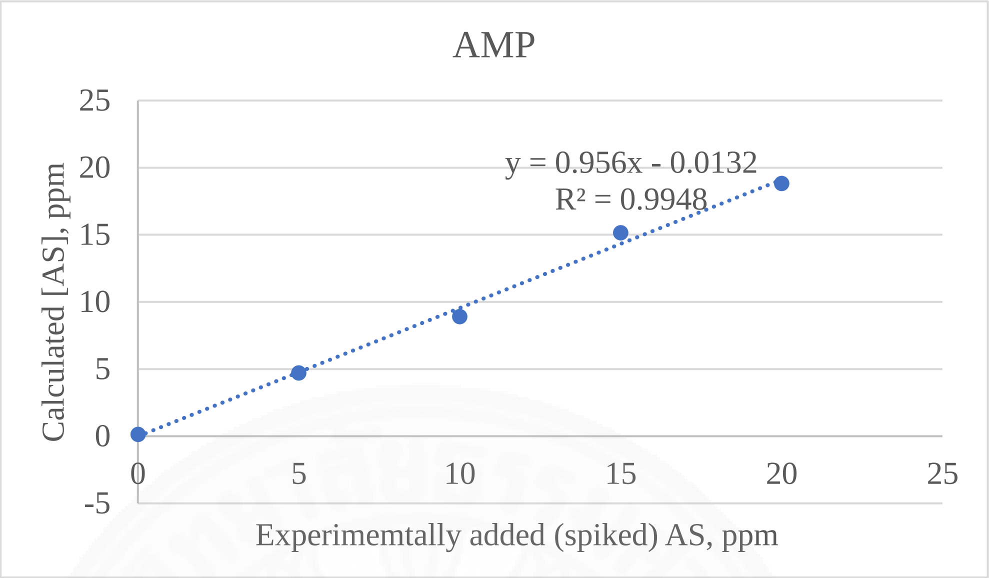
The result from the experimentally added AS concentration and calculated AS concentration from the model of make-up water was then plotted to see the relation of these values as shown in figure 4.24 (a), (b). It can be seen from the plot that the predicted increase in AA/AMPs or PMA concentration follows quite well as the experimental increase (spike) in the AA/AMPs and PMA. The linear relation between the added amount and the measured amount was obtained with the slope of 0.956 and 0.948 for AA/AMPs and PMA, respectively. Extrapolating the graph to the zero concentration yields the value of 0.01 ppm and 0.54 ppm, which is predicted value of the active AA/AMPs and PMA in the make-up water that considered as free AS water sample.

The result from the calculation of spiked mixture component at 5 ppm for both AA/AMPs and PMA in make-up water sample was 5.68 ppm and 7.58 ppm for AA/AMPs and PMA, respectively. In case of spiked AA/AMPs 15 ppm and PMA 5 ppm, the result was 18.69 ppm and 4.64 ppm for AA/AMPs and PMA, respectively. In case of spiked AA/AMPs 15 ppm and PMA 5 ppm, the result was 8.14 ppm and 12.01 ppm for AA/AMPs and PMA, respectively.

From the spiked test result in make-up water, the development technique yielded the calculation value of AS concentration quite close to the actual value of spiked known amount of AS in the experiment. As the result, the development technique can be confirmed to give the accuracy of anti-scalant concentration for analysis.

Table 4.9 The spiked concentration determination analysis of the make-up water

Sample	Spiked [AS], ppm	Absorbance at 320 nm		[AS] calculation, (ppm)	
		HI 100 ppm	HI 300 ppm	AA/AMPs	PMA
Pure make-up water	0	0.003	0.01	0.14	0.18
Spiked AA/AMPs in make-up water	5	0.099	0.197	4.72	1.48
	10	0.188	0.332	8.90	1.49
	15	0.32	0.495	15.14	0.18
	20	0.398	0.7	18.83	3.05
Spiked PMA in make-up water	5	-0.021	0.132	-0.99	5.50
	10	-0.027	0.301	-1.26	11.44
	15	0.052	0.458	2.44	12.69
	20	0.056	0.692	2.66	20.29
Spiked AA/AMPs and PMA	AA/AMPs 5 ppm PMA 5 ppm	0.12	0.41	5.68	7.58
	AA/AMPs 15 ppm PMA 5 ppm	0.395	0.743	18.69	4.84
	AA/AMPs 5 ppm and PMA 15 ppm	0.172	0.622	8.14	12.01



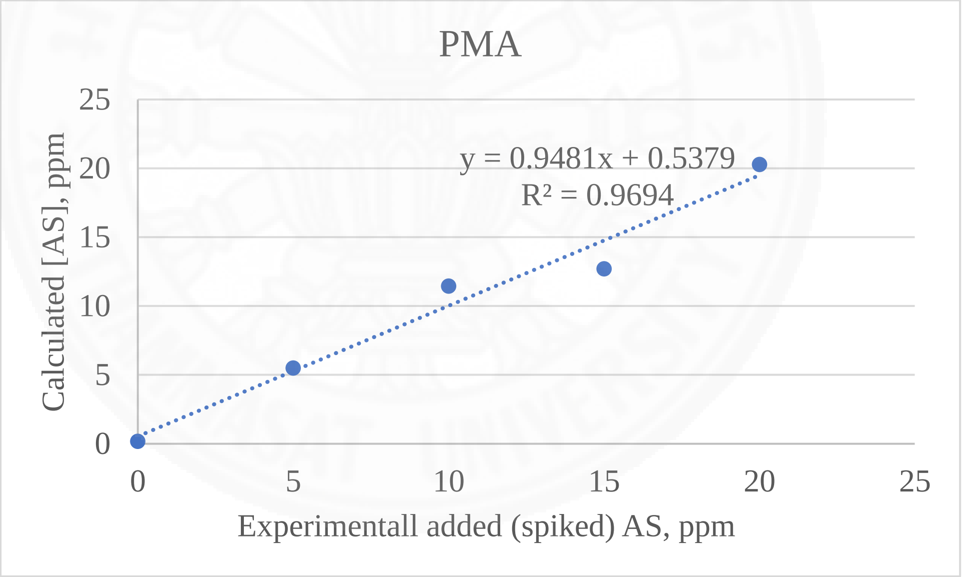


Figure 4.24 The correlation between the calculated AS concentration and the experimentally added AS concentration of the make-up water using HI 100 and 300 ppm; (a) AA/AMPs and (b) PMA

CHAPTER 5
SUMMARY

The development technique for anti-scalant concentration determination was achieved via the polymer-surfactant complexation system. The technique was considered as a simple mixed technique that can be used in the cooling system field conveniently. AA/ AMPs poly(acrylic acid:2-acrylamido-2-methylpropane sulfonic acid) and PMA (polymaeic acid) were a carboxylic anti-scalant that typically used to prevent a scale formation and disperse a scale forming. Benzethonium chloride (HI) was utilized as a cationic surfactant that can be bonded with oppositely charge anti-scalant due to the electrostatic and hydrophobic interaction. The absorbance was collected for anti-scalant concentration calculation. Turbidity was measured to confirm the complexation between these two types of chemicals.

As the result of using 100 ppm of Hyamine, the absorbance and turbidity were increased as significantly in case of AA/AMPs compared to PMA. Moreover, increasing PMA concentration to 80 ppm resulted in an increased absorbance and turbidity almost the same as AA/AMPs at 20 ppm. Hence, using only 100 ppm of Hyamine was not suitable in order to separate the difference between AA/AMPs at low concentration and PMA at high concentration.

The technique was utilized two concentrations of Hyamine for concentration calculation of these two typed of anti-scalants. Hyamine at 300 ppm was selected for the analysis because it was obtained the maximum absorbance and turbidity. Zeta potential result was confirmed the complete binding in polymer-surfactant system at 300 ppm.

The absorbance of AS-HI depended on the calcium ion concentration that contained in the water sample. As the result, the specific coefficient was suggested to calculate for anti-scalant concentration analysis.

In addition, this technique is not interfered by the presence of sulfate or PBTC, another commonly added chemical, can be applied for analysis of AA/AMPs and/or PMA in the actual cooling system.

The concentration of active polymer in the system can be determined via the complexation with the positively charged Hyamine and measured via the UV-Vis spectroscopy. The coefficient at 100 ppm (or 150 ppm) and 300 ppm of Hyamine for complexation can be used to estimate the concentration of AA/AMPs and/or PMA in the actual cooling water sample.

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APPENDICES

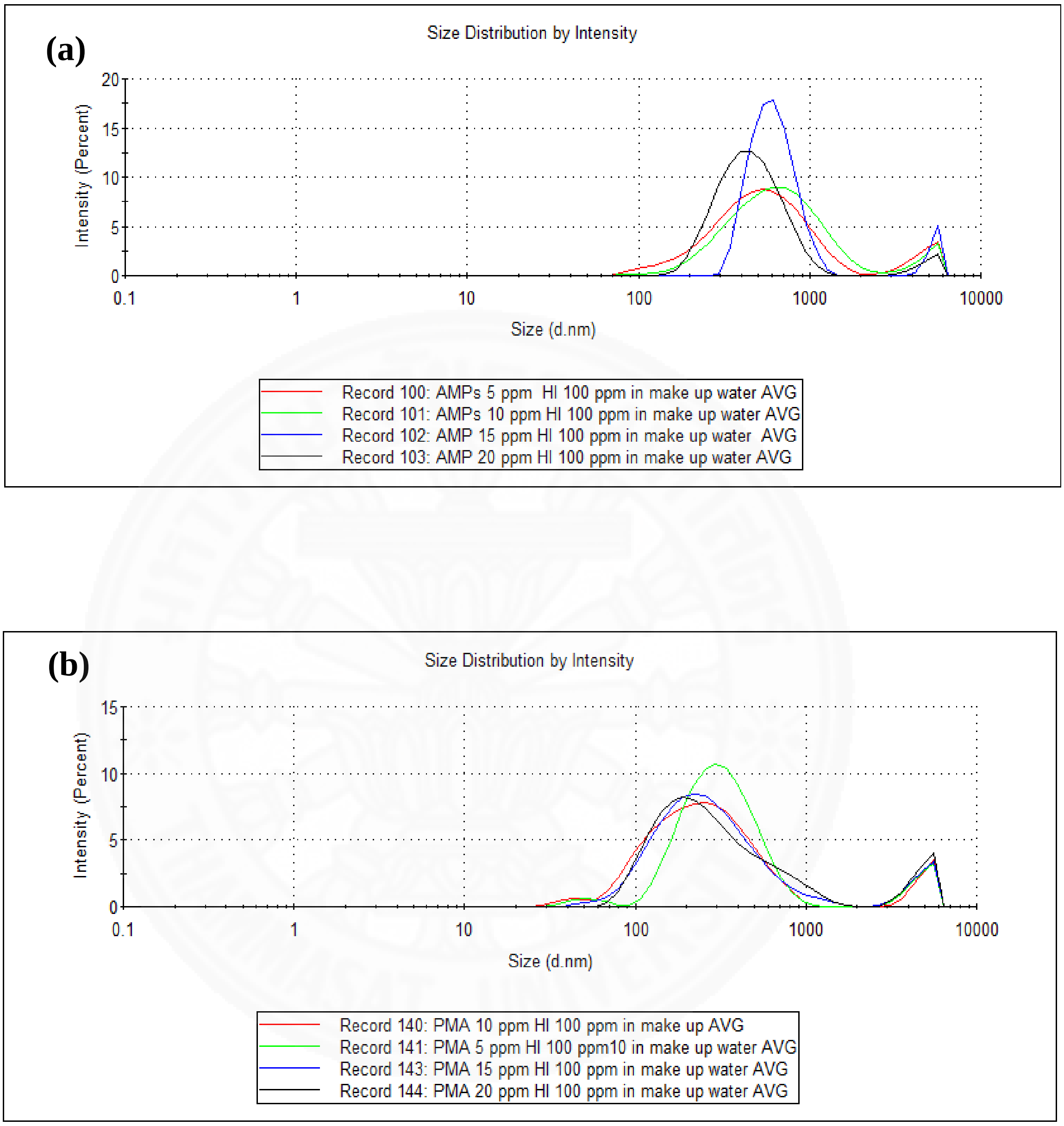
APPENDIX A

Characteristics of complexed particle (HI 100 ppm and 300 ppm)

Particle size of various concentrations of AA/AMPs and PMA mixed with HI at 100 ppm

Anti-scalant concentration (ppm)	AA/AMPs (ppm)			PMA (ppm)		
	Size average (nm)	PDI	Quality report	Size average (nm)	PDI	Quality report
5	490.7	0.438	Good	297.3	0.451	Good
10	626.6	0.399	Good	231.0	0.487	Good
15	1000	0.546	***	258.0	0.480	Good
20	434.1	0.303	Good	259.4	0.542	Good

*** = Refer to quality report, that has some large or sediment particles. Sample is too polydisperse for distribution analysis



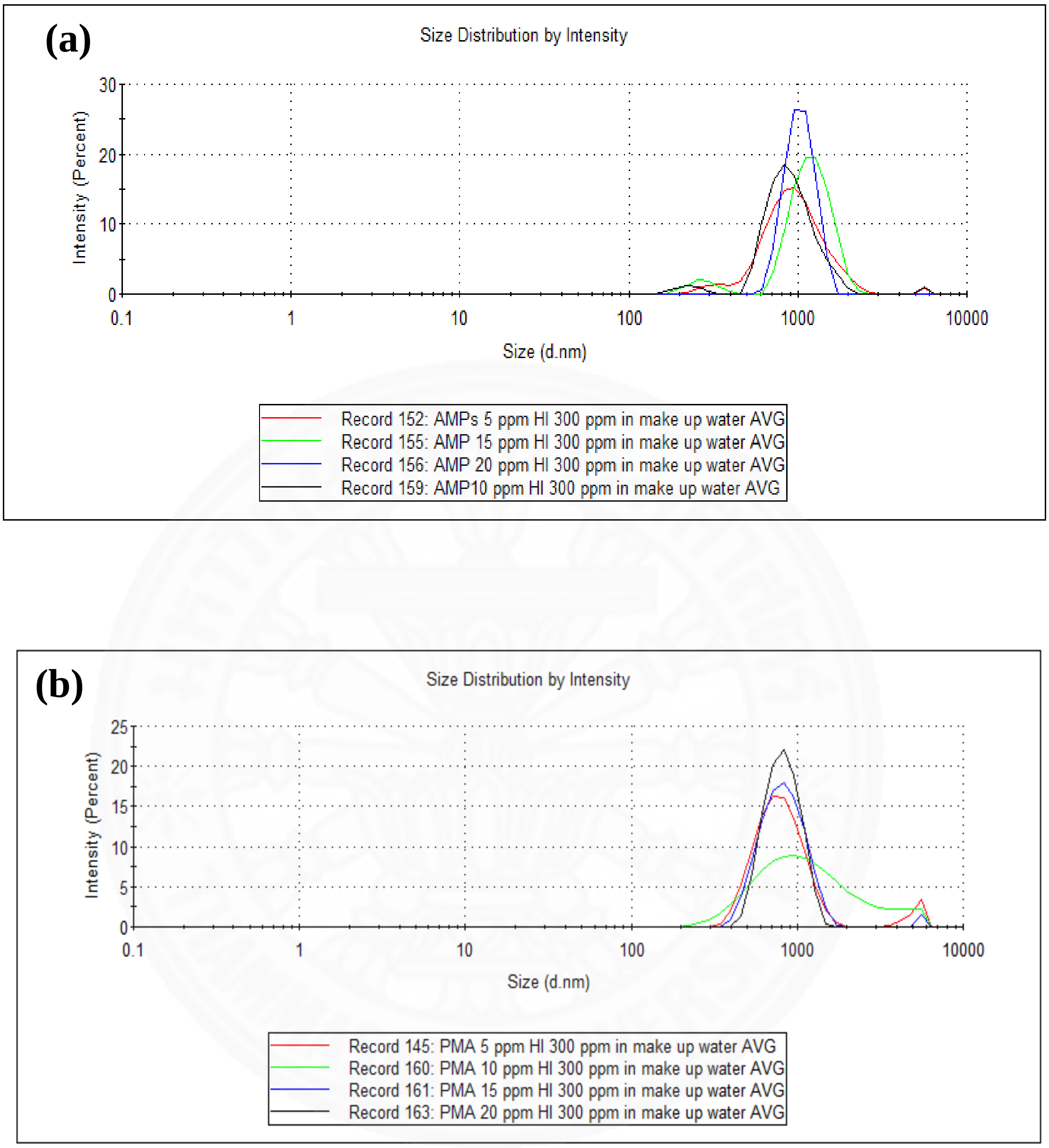
Size distribution by intensity of Hyamine 100 ppm with;

(a) AA/AMPs and (b) PMA

Particle size of various concentrations of AA/AMPs and PMA mixed with HI at 300 ppm

Anti-scalant concentration (ppm)	AA/AMPs (ppm)			PMA (ppm)		
	Size average (nm)	PDI	Quality report	Size average (nm)	PDI	Quality report
5	1062	0.464	***	856.9	0.379	Good
10	1144	0.439	***	938.2	0.350	Good
15	1473	0.506	***	948.0	0.350	Good
20	1769	0.566	***	1000	0.390	***

*** = Refer to quality report, that has some large or sediment particles. Sample is too polydisperse for distribution analysis



Size distribution of Hyamine 300 ppm with;

(a) AA/AMPs and (b) PMA

APPENDIX B

Effect of HI at difference concentration to AS (AA/AMPs or PMA) at 20 ppm

Surfactant concentration (ppm)	AA/AMPs				PMA			
	Avg. Size (nm)	PDI	Result Quality	Turbidity (NTU)	Avg. size (nm)	PDI	Result Quality	Turbidity (NTU)
0	996.2	0.763	***	1.2	423.1	1	***	0.91
50	136.3	0.213	Good	19.3	514.0	0.481	Good	5.83
100	200.8	0.105	Good	85	328.4	0.322	Good	34.4
200	809	0.298	Good	92.1	1169	0.49	***	74.6
300	1396	0.523	***	99.5	1712	0.64	***	87.1
400	508.1	0.561	Good	87.8	1857	0.756	***	85.6
500	251.4	0.502	Good	79.7	1053	0.683	***	72.5
600	171.5	0.301	Good	58.5	303.4	0.498	***	50.9
700	152.5	0.296	Good	28.7	210.1	0.44	Good	32.9

*** = Refer to quality report, that has some large or sediment particles. Sample is too polydisperse for distribution analysis

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