

***Synthesis of Poly (Acrylic Acid-Co-Sodium Styrene Sulfonate) as Scale Inhibitor
for Industrial Cooling Water System***

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Abstract

Water from most natural sources usually contains dissolved minerals and scale forming ions such as Ca^{2+} and Mg^{2+} ions. Poly (acrylic acid) (PAA) is one of the scale inhibitor polymers, commonly used in the industrial circulating cooling water system. However, the remaining polymer concentrations of scale inhibitors are facing some level of difficulty for determination. This is mainly due to the fact that there is a similar range of UV adsorption to another organic compound in the cooling water system. For that, the modification of PAA to copolymer of acrylic acid and sodium styrene sulfonate (NaSS) are being thoroughly investigated. Poly (acrylic acid-co-sodium styrene sulfonate) are synthesized by a free radical polymerization procedure under the water solution technique being performed, together with potassium persulfate as a free radical initiator. The synthesized copolymers are confirmed by $^1\text{H-NMR}$, FTIR and UV-Vis Spectroscopy. As such, the molecular weights of PAA-co-NaSSs are characterized by $^1\text{H-NMR}$ and thermal analysis data are also being conducted by a TGA. Concentration of polymer dosages at 20, 30, 40, 50, 60, 80 and 100 ppm are consecutively tested in supersaturated calcium ion (400 ppm) and bicarbonate ion (500 ppm) solutions at a temperature of 70°C for a time period of 24 hours. Most importantly, the performance of PAA-co-NaSS on complexes with Ca^{2+} and ratio of scale inhibitor are also being studied.

Keywords: Poly(acrylic acid-co-sodium styrene sulfonate), Scale inhibitor, Cooling water system

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Introduction

Cooling water system is water to control the temperature of machine or processes to lower temperature by transferred heat from machine or processes to the coolant. (Hill, Pring, & Osborn, 1990; Frayne, 1999; Herro, & Port, 1993). In the industrial cooling systems today, use of water from the river as the source material is common such as calcium and magnesium ions. Under conditions of temperature, pH, pressure, dissolved mineral etc., relatively insoluble species such as carbonates and sulphates may deposit from solution as scale. When scale problems occur on the surface of the cooling system leads to reduction in heat transfer, clogging of filters, reduces the flow rate, loss of system performance and complete shutdown of the installation.

Generally this water needs to be purified before it can be used in the process. However, when the water circulating in the system indefinitely. Require water treatment such as blowdown or ion-exchange regeneration effluents or additional chemical into the processes as an alternative to solve the problems of fouling and corrosion in the system. There are water-soluble molecules or polymers with several functional groups, the most common groups being phosphates. Although, phosphates are highly efficient as a scale inhibitor, which cause of the Eutrophication phenomenon. Thus, the polymer additives category is the way to control water quality, quantity of ion in the appropriate level. Polymer could react with cation contained in the water, especially Ca^{2+} and Mg^{2+} occur as complex compounds and removed from the manufacturing process by precipitation processes. (Chuang et al., 2013; Volkringer et al., 2007).

Polymer used to control water quality in many species, such as poly (maleic acid) and poly (acrylic acid) due to chemical structures and functional groups that assist in create a bond with the metal ions. (Amjad, & Koutsoukos, 2014; Martinoda, Euvrard, Foissyb, & Neville, 2008). However, the polymer used to control water quality in recirculating cooling water systems must be able to measure the amount of polymer used. Polymer of each plant will require a set of measurements that are highly specific of the factory and cannot use a series of sensors with polymer type, so the remaining polymer concentrations of scale inhibitors are facing some level of difficulty for determination.

In this work, focuses on the quantitative analysis of polymer remaining in the cooling water systems. The scale inhibitor synthesis between acrylic acid and sodium styrene sulfonate, were tested with respect to their ability to inhibit calcium carbonate.

Material and Experimental

Materials

Acrylic acid, Sodium 4-vinylbenzene sulfonate, Calcium chloride and Sodium bicarbonate were supplied by Sigma-Aldrich Co. LLC., USA. Potassium persulfate was purchased from Ajax Finechem Pty. Ltd., Australia. Magnesium chloride and Disodium EDTA were product from Merck KGaA, Germany.

Synthesis of PAA-co-NaSS

Acrylic acid (AA) : sodium 4-vinylbenzene sulfonate (NaSS) (5:5, 6:4, 7:3, 8:2 and 9:1 by weight, respectively) and potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) were dissolved in 100

ml of distilled water in a two-neck round-bottom flask (250 ml) equipped with a condenser and an inlet of dry nitrogen. (Weiss, Turner, & Lunberg, 1985). The ratio of synthetic polymer is summarized in Table 1. The reaction proceeded with continuous stirring at 70°C for 3 hr. The solution was stop reaction by 10 ml of methanol. Then, bottle was stirring for 5 min. Spread the product on a petri dish and dry in oven at 70°C for 12 hr. Chemical structure, molecular weight and residual of polymer were characterized by FTIR, ¹H NMR, and UV-Visible spectrophotometer, respectively.

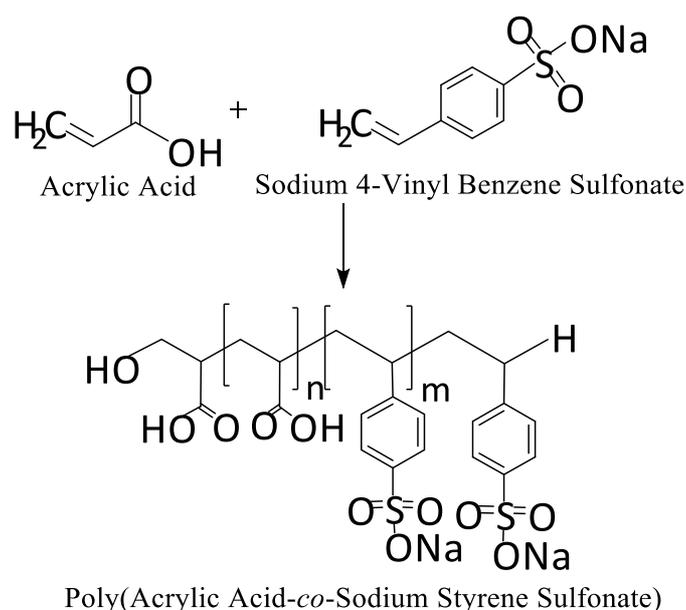


Figure 1: Preparation of PAA-co-NaSS.

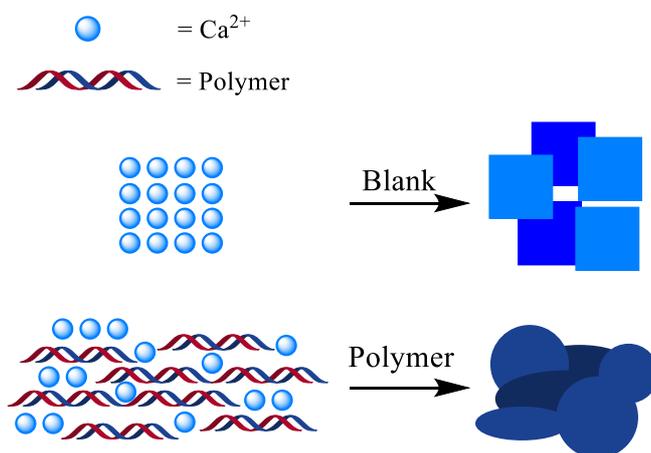


Figure 2: Schematic diagram of the effect of Polymer on the morphology of calcium carbonate crystals.

Table 1: Ratio of synthetic polymer between AA, NaSS and K₂S₂O₈

Polymer	AA (g)	NaSS (g)	K ₂ S ₂ O ₈ (g)
PAA	10	0	0.1666
PNaSS	0	10	0.0203
PAA-co-NaSS-155	5	5	0.2105
PAA-co-NaSS-164	6	4	0.2534
PAA-co-NaSS-173	7	3	0.2998
PAA-co-NaSS-182	8	2	0.3501
PAA-co-NaSS-191	9	1	0.4042
PAA-co-NaSS-255	5	5	0.0758
PAA-co-NaSS-264	6	4	0.0912
PAA-co-NaSS-273	7	3	0.1079
PAA-co-NaSS-282	8	2	0.1260
PAA-co-NaSS-291	9	1	0.1455
PAA-co-NaSS-355	5	5	0.0189
PAA-co-NaSS-364	6	4	0.0228
PAA-co-NaSS-373	7	3	0.0270
PAA-co-NaSS-382	8	2	0.0315
PAA-co-NaSS-391	9	1	0.0364

Scale inhibition method

Calcium inhibition was studied in artificial cooling water which was prepared by dissolving a quantity of CaCl₂ and NaHCO₃ in distilled water as concentrations of Ca²⁺ and HCO₃⁻ were 400 and 500 mg·L⁻¹, respectively. Then, add polymer at dosage 20, 30, 40, 50, 60, 80 and 100 ppm in the artificial cooling water adjusted at 70°C for 24 hr.

The performance of the tested compounds as calcium carbonate inhibitor was calculated using eq. (1).

$$\%CaCO_3 \text{ inhibition} = \frac{\text{EDTA Sample (ml)} - \text{EDTA Blank (ml)}}{\text{EDTA Standard (ml)} - \text{EDTA Blank (ml)}} \times 100 \quad (1)$$

Where: EDTA Sample was the concentrations of Ca²⁺ (mg·L⁻¹) in the filtrate in the presence of an inhibitor at 24 hr.

EDTA Blank was the concentrations of Ca²⁺ (mg·L⁻¹) in the filtrate in the absence of an inhibitor at 24 hr.

EDTA Standard was the total concentrations of Ca²⁺ (mg·L⁻¹).

Results and Discussion

Characterization of PAA-co-NaSS

Molecular structures of AA, PAA and PAA-co-NaSS characterized by FTIR were compared in fig. 3 and fig. 4, taken over the range of wavenumber from 400 to 4000 cm^{-1} . In case of PAA, the new peaks at 1714 cm^{-1} corresponding to C=O stretching, appear clearly. Moreover, the missing peak of C=C stretching at 1635 and 1616 cm^{-1} of AA and turn to be single bond in the main structure of PAA. (Moulay, & Mehdaoui, 2004). But for the analysis of PAA-co-NaSS, spectra are shown over the range from 3200 to 3550 cm^{-1} which is belonging to O-H stretching of aromatic and the absorption at approximately 1475 and 1600 cm^{-1} result from a C=C stretching vibration of aromatic.

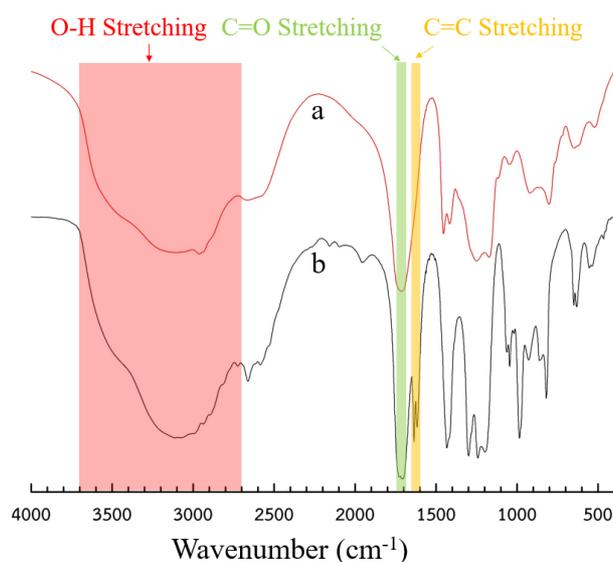


Figure 3: FTIR spectra (a) PAA, (b) AA

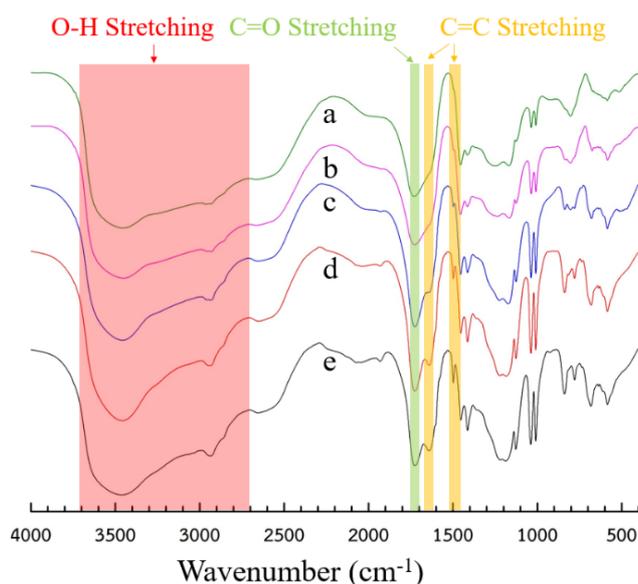


Figure 4: FTIR spectra (a) PAA-co-NaSS-391, (b) PAA-co-NaSS-382, (c) PAA-co-NaSS-373, (d) PAA-co-NaSS-364 and (e) PAA-co-NaSS-355

The chemical structure of PAA and PAA-co-NaSS were studied by UV-vis spectroscopy, carried out in water and results are shown in figure 5. UV-vis spectra of acetic acid and sodium styrene sulfonate were also used to identify the structure of PAA and PAA-co-NaSS. Absorptions at 200 and 256 nm correspond to the benzene ring absorption of sodium styrene sulfonate and acetic acid as shown the carboxylic at 210 nm. The absorption of PAA at 210 nm, the fact that organic compounds are generally the absorption wavelength in this range. The remaining polymer concentrations of scale inhibitors are facing some level of difficulty for determination. In case of PAA-co-NaSS, the 210 nm peak shifts to 225 nm corresponding to overlap of carboxylic and benzene ring. The 225 and 256 nm peak increase, when higher amount of NaSS.

The relationship between PAA-co-NaSS intensity and the concentration is shown in fig. 5, provides an almost linear response (correlation coefficient $r = 0.9991-0.9999$). This positive linear relationship could be used to quantitatively measure the concentration of PAA-co-NaSS in cooling water system.

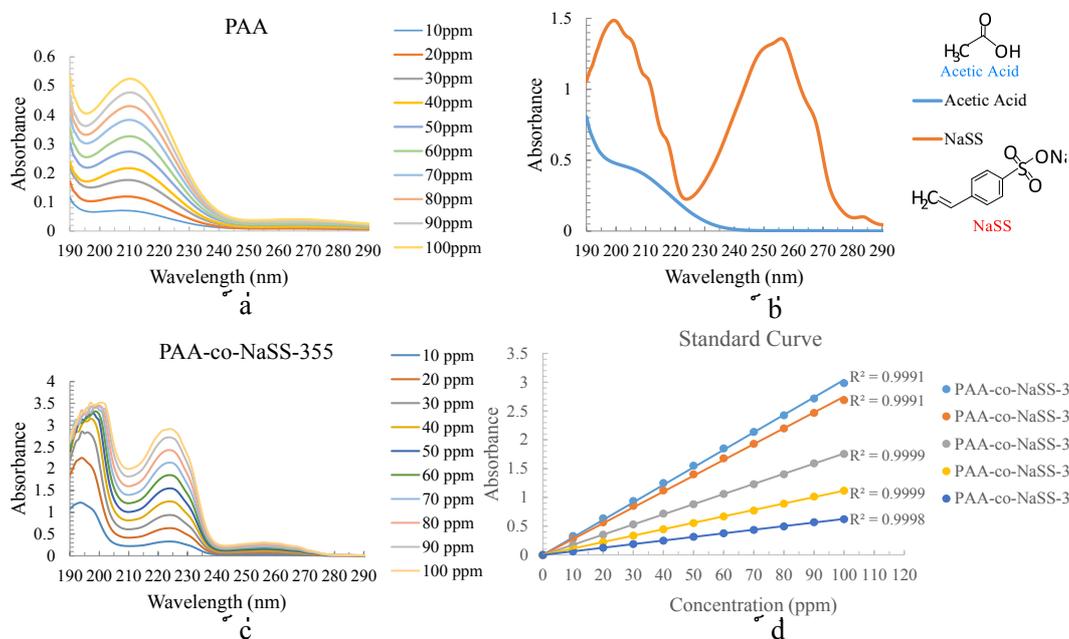


Figure 5: UV-Visible spectra (a) PAA, (b) Acetic acid and NaSS, (c) PAA-co-NaSS-355 and (d) Relationship between PAA-co-NaSS intensity and the concentration of PAA-co-NaSS-355

The ability to the complexation of PAA-co-NaSS with Ca^{2+} can be determined by percent of scale inhibition. Fig. 6 and 7 show calcium inhibition as the different concentration of PAA, PNaSS, PAA-co-NaSS and mixed between PAA and PNaSS (PAA+PNaSS) from 20 to 100 ppm at 70°C. Solution of PAA and PAA+PNaSS are turbidity and scale deposits around the bottle as well as PNaSS, but solution of PNaSS is clearer. While PAA-co-NaSS is the clearest. (Wang, Cölfen, & Antonietti, 2005). PAA, PNaSS and PAA+PNaSS exhibited an ability to control scale, with 35% Ca^{2+} inhibition at 20 ppm, 60% for 100 ppm. Scale inhibition effect were in a similar linear increasing trend with increasing the polymer concentration, when the PAA-co-NaSS dosing changed at the range of 20-100 ppm, scale inhibition increased from 60-100%.

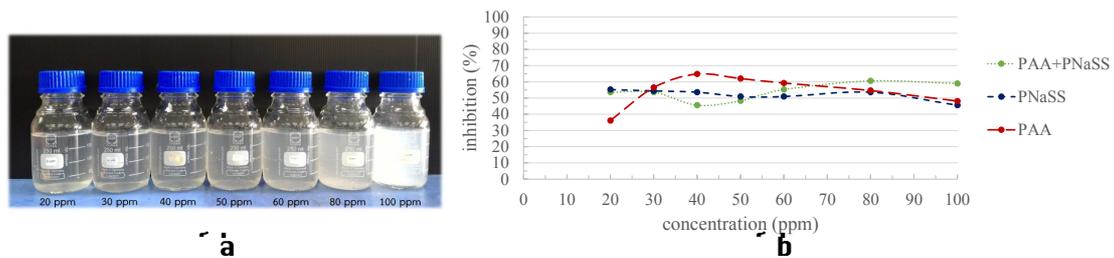


Figure 6: (a) Solution of PAA with the concentrations of Ca^{2+} and (b) percent inhibition PAA, PNaSS and PAA+PNaSS

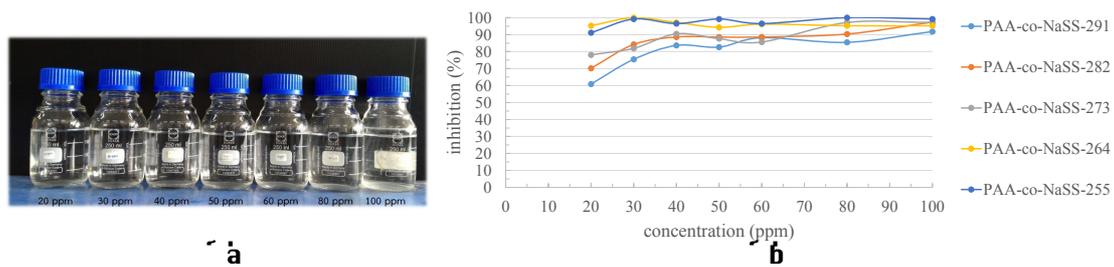


Figure 7: (a) Solution of PAA-co-NaSS with the concentrations of Ca^{2+} and (b) percent inhibition PAA-co-NaSS-291, PAA-co-282, PAA-co-NaSS-273, PAA-co-NaSS-264 and PAA-co-NaSS-255

Conclusion

In this research study to prepare poly (acrylic acid-co-sodium styrene sulfonate) through a free radical polymerization, and then implemented in the scale inhibition caused by calcium ion. The structure of synthesized copolymers are characterized by $^1\text{H-NMR}$, FTIR and UV-Vis Spectroscopy. The correlation coefficient of PAA-co-NaSS was 0.9999 and the scale inhibition efficiency at the range 80-100% when the dosage was 40-100 ppm.

References

Amjad, Z., & Koutsoukos, P. G. (2014). Evaluation of maleic acid based polymers as scale inhibitors and dispersants for industrial water applications. *Desalination*. 335, 55-63.

Chuang, E., Lin, K., Su, F., Chen, H., Maiti, B., Ho, Y., et al. (2013). Calcium depletion-mediated protease inhibition and apical-junctional-complex disassembly via an EGTA-conjugated carrier for oral insulin delivery. *Journal of Controlled Release*. 169, 296-305.

Frayne, C. (1999). *Cooling water treatment: Principles and practice*. New York: Chemical.

Herro, H. M., & Port, R. D. (1993). *The Nalco guide to cooling water system failure analysis*. New York: McGraw-Hill.

Hill, G. B., Pring, E. J., & Osborn, P. D. (1990). *Cooling towers: Principles and practice*. (3rd ed.). London: Butterworths.

Martinoda, A., Euvrard, M., Foissyb, A. & Neville, A. (2008). Progressing the understanding of chemical inhibition of mineral scale by green inhibitors. *Desalination*. 220, 345-352.

Moulay, S., & Mehdaoui, R. (2004). Hydroquinone/catechol-bearing polyacrylic acid: Redox polymer. *Reactive and Functional Polymers*. 61, 265-275.

Volklinger, C., Loiseau, T., Ferey, G., Warren, J. E., Wragg, D. S., & Morris, R. E. (2007). A new calcium trimellitate coordination polymer with a chain-like structure. *Solid State Sciences*. 9, 455-458.

Wang, T., Cölfen, H., & Antonietti, M. (2005). Nonclassical crystallization: Mesocrystals and morphology change of CaCO₃ crystals in the presence of a polyelectrolyte additive. *Journal of the American Chemical Society*. 127, 3246-3247.

Weiss, R. A., Turner, S. R., & Lunberg, R. D. (1985). Sulfonated polystyrene ionomers prepared by emulsion copolymerization of styrene and sodium styrene sulfonate. *Journal of Polymer Science*. 23, 525-533.

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