Synthesis of Hydrophilic Polyelectrolyte as Draw Solute for Forward Osmosis Process

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ABSTRACT

Synthesis and characterization of hydrophilic polyelectrolyte was performed in this work and used as draw solute for forward osmosis (FO) process. The effect of different ratios of acrylic acid (AA) and benzoyl peroxide (B) on the properties of polyelectrolyte was studied in this work. The physical and chemical properties of draw solution (DS) such as pH, conductivity, osmolality, viscosity, molecular weights and functional group were investigated. Results showed that the solution osmolality increased with increasing AA/B ratio. Self-synthesized polyelectrolytes with different molecular weights (MWs) were further correlated with its solution osmolality. The self-synthesized polyelectrolytes of PAA-K and PAA-Na showed an increasing of hydrophilic functional groups such as –OH or COOH. PAA-Na with lower MW and high osmotic pressure in the aqueous solution is found to exhibit a lower reverse solute flux during FO process. Meanwhile for the polyelectrolyte with higher MW, higher viscosity and lower diffusion coefficient were reported.

Keywords: Forward osmosis, draw solution, polyelectrolyte, reverse solute flux, diffusion

1.0 INTRODUCTION

Forward osmosis (FO) is one of the membrane separations technology for water reuse and desalination. The FO has naturally driven force use osmotic pressure difference across a semi-permeable membrane process [1-4]. Compare FO processes to hydraulic pressure process is more advantage such as low energy consumption and low membrane fouling [5]. There are three components in the FO system. Firstly, the membrane type is important to fabric and modify the high hydrophilic membrane [1]. Secondly, draw solution (DS) is a solution with high osmotic pressure. Finally, the recovery method of DS is the process to maintain a constant concentration of DS, which is commonly used by a membrane

separation process such as Nanofiltration, ultrafiltrationn membrane distillation, etc [6-8]. Several solutions have been used for DS for instance NaCl, $MgCl_2$, KNO_3, $MgSO_4$, sucrose, ammonium bicarbonate (NH_4HCO_3) ammonium hydroxide (NH_4OH). Lutchmiah *et al*. [8] reported that NaCl is a favored solution used for DS amount 40%. The criteria to consider the selection of the DS by Achilli *et al*. [9] is high water solubility, high flux obtain, high osmolality, lower salt leakage, low energy for recovery and stability after recovery.

Researchers have investigated the use of inorganic salts as draw solutions due to low cost and high osmotic pressure potential, which creates a high water flux. Hydrophilic magnetic nanoparticle (MNP) has been used as a

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draw solution with high osmotic and high water flux and easy to recycle of draw solute [4, 6] In addition, other materials have been used for FO. Ge *et al*. [4] have studied the different molecular weights of the sodium salt of polyacrylic acid (PAA-Na). It presented the solute with the lowest molecular weight that obtained the maximum FO flux due to its low viscosity and high dissociation. Nguyen *et al*. [10] studied FO process with 0.1 M EDTA-2Na coupled with 15 mM NP7 as a draw solution. The results showed that the lowest reverse salt flux was observed due to the hydrophobic interaction between the tails of NP7 and the FO membrane. Kumar *et al*. [11] synthesized the hydrolyzed poly (isobutylene-alt-maleic acid) (PIAM-Na) and used as draw solute for FO desalination. Huang *et al*. [12] employed P(SSA-co-MA)-Na as a novel draw solute in FO process and showed high water flux. Nevertheless, the main problem of draw solutions show reasonable water flux but high reverse salt flux (RSF) [10, 12]. Salt leakage is occurred by the accumulation of concentration or internal concentration polarization (ICP). That is based on the diffusion-convection transport of draw solution in the support layer [3]. The objective of this work is to synthesize new type of polyelectrolyte and use it as draw solute for FO process. It is expected that the draw solution could achieve high osmotic pressure and high water flux without minimum low reverse salt

leakage.

2.0 METHODS

2.1 Materials

Acrylic acid (AAc, purity 99%, 200 ppm monomethyl ether hydroquinone as inhibitor) was obtained from LobaChemie, Mumbai, India. Ethanol (purity 99.99 %) was purchased from RCI lab scan Limited, Thailand. Benzoyl Peroxide (98%, humidified with 25% of H_2O PS) was acquired from Panreac Quimica S.L.U., Spain. Sodium hydroxide (NaOH, purity 99%) was purchased from Merck, Germany. Potassium hydroxide (KOH, purity 85 %) was achieved from Ajax Finechem, Australia. Acetone (purity 99.5 %), Surfactant (Triton™ X-114) and PAA-Na (1200) were purchased from Sigma-Aldrich, UK. Membrane TFC was supplied from HTI (Hydration Technologies Inc., OR, USA).

2.2 Preparation of PAA

AAc 15 ml and acetone 150 ml were mixed at 110 °C, before adding 10 g of benzoyl peroxide and stirred well for 90 min. The final PAA mixture was dried in vacuum at 100 °C for 30 min. The reaction of synthesis polymerization of acrylic acid was shown in Figure 1.
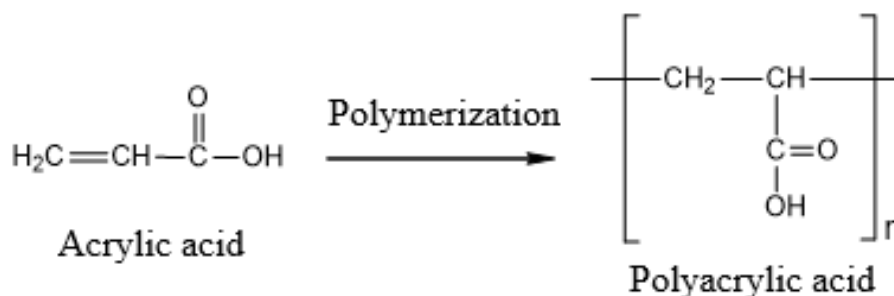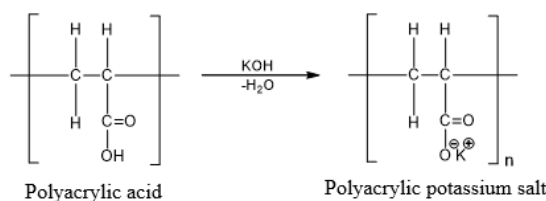

Figure 1 The reaction of polymerization of polyacrylic acid

2.3 Synthesis of PAA-K and PAA-Na

The preparation of PAA-K was taken PAA amount 10 g (From 2.2) and was mixed with 3.5 g of KOH then dissolved in 100 ml of ethanol. Surfactant (Triton™ X-114) 0.026 %w/v was added and stirred well mixing for 30 min at room temperature. The final product of

PAA-K was obtained after filtrated and dried in the vacuum oven. For the preparation of PAA-Na, was also prepared using the same procedure except NaOH used instead of KOH. The initial concentration of each polyelectrolyte for the characterization was used at 0.48 g.mL^{-1} [7]. The reaction of synthesis of the polyelectrolytes salt is shown in Figure 2.
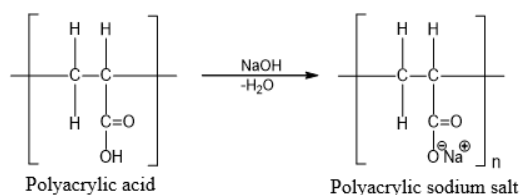
PAA-K

PAA-Na

Figure 2 The reaction of synthesis of the polyelectrolytes; PAA-K and PAA-Na

2.4 Characterization of PAA

The characterization of PAA, the chemical functional group was analyzed by Attenuated Total Reflectance- Fourier transform Infrared spectroscopy, ATR-FTIR (Tensor 27, Bruker, US). The pH was tested by pH meter (Cyberscan Pc 300, Eutech instruments). Conductivity was measured by conductivity meter (WTW, LF318, Germany). The osmolality was measured by Osmometer (Fiske Associates 210, Massachusetts, USA). The viscosity of PAA-Na and PAA-K were measured by viscometer (Brookfield, USA). The molecular weight of self-synthesized polyelectrolytes analyzed by Liquid Chromatography Mass Spectrometer

(LCMS, Q-TOF 6545 Agilent Technologies, USA).

2.5 Membrane Permeability and DS Testing in FO Process

A lab-scale FO system was employed for all FO tests. The commercial thin film composite (TFC) FO membrane from HTI (Hydration Technologies Inc., OR, USA) was used in this work. The FO module was made from Acrylic plastic with 15 cm. length, 5 cm. width, and 0.3 cm. depth for each side. NaCl, PAA-Na and PAA-K were used as the draw solutions and DI water was used as the feed solution. During the FO test, both feed and draw solutions operated at a fixed volumetric flow rate (100 ml/min) at

room temperature (25 ±1 °C) in co-current mode. Ultrafiltration was used for the recovery process. For UF experiments, polyvinylidene difluoride (PVDF) hollow fiber membrane (Steritech, USA) of 0.05 mm pore size was operated under pressure of 5 bars. The schematic of laboratory scale is presented in Figure 3. The water flux (Jw, L/m^2·h, referenced to as LMH) was measured from the weight of permeate and calculated following *Eq. (1)*.

$$J_w = \frac{\Delta weight}{water\ density \times effective\ membrane\ area \times \Delta time} \quad (1)$$

The reverse solute flux, RSF (*Js*, g/m^2·h, referenced to as gMH) was measured based on the calibration curve of the conductivity versus the polyelectrolytes salt concentration. The RSF was determined using *Eq. (2)*.

$$Js = \frac{\Delta CtVt}{A\Delta t} \quad (2)$$

where *Ct* (g/L) and *Vt* (L) are the reverse solute concentration and the volume of the feed solution, respectively, at an arbitrary time *t* [11]. Number of recovery cycle were determined for water flux (*J*, LMH) production after filtrated by ultrafiltration.
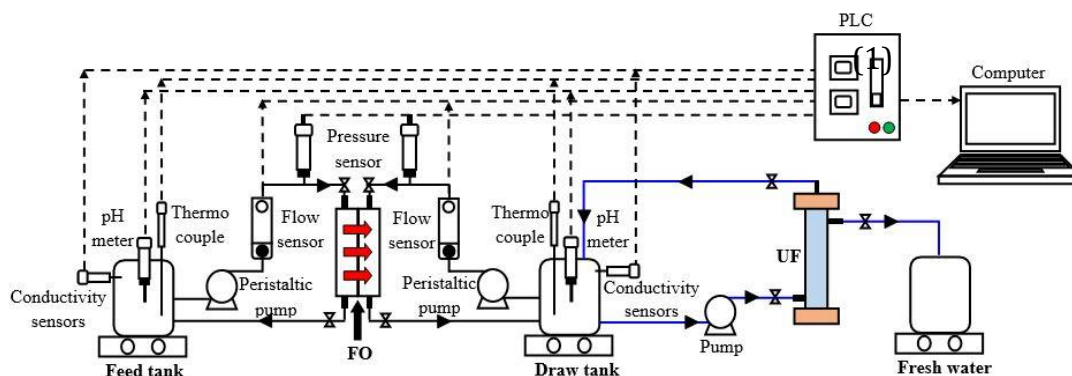

Figure 3 The schematic of laboratory scale

3.0 RESULTS AND DISCUSSION

3.1 Characterization

3.1.1 Functional Group of PAA, PAA-K and PAA-Na

FTIR-ATR spectrum of synthetic polyelectrolytes (Figure 4) showed the strong peak at wavenumber 3,422 cm^{-1} and 3,428 cm^{-1} (O-H stretching) of hydroxyl group for PAA-K and PAA-Na, respectively. The FTIR spectra showed the increasing of hydrophilic functional group such as –OH group, formed after the polymerization of polyelectrolytes. In addition for PAA-Na, showed the shoulder peaks of C=C and C=O attributed to carboxylic acid groups. These results are similar to Kumar *et al*. [11] that demonstrated these peaks after the hydrolysis of anhydride.
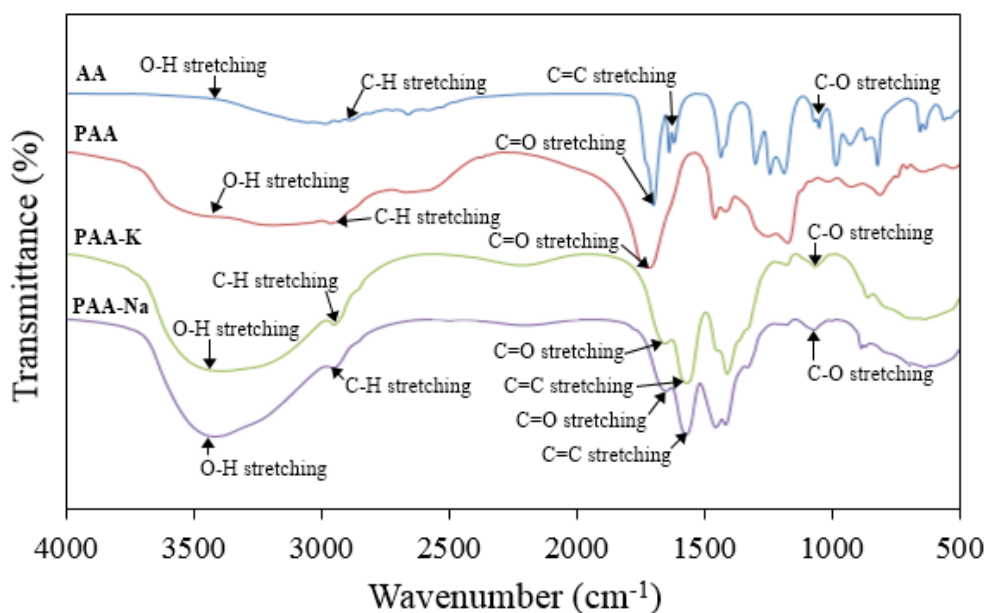
Figure 4 ATR-FTIR spectra of; PAA, PAA-K, PAA-Na

3.1.2 pH of PAA, PAA-K and PAA-Na

pH value of self-synthesized polyelectrolytes (Figure 5), they were 2.6 (acidity), 9.3 (alkalinity) and 7.1 (neutral) for PAA, PAA-K and PAA-Na, respectively. The self-synthesized polyelectrolytes of PAA-Na showed neutral pH that similar to the commercial PAA-Na is equal to 7.1.

These results presented that self-synthesized PAA-Na is suitable to use in the FO process. The FO membrane such as cellulose triacetate membrane (CTA) and thin film composite membrane (TFC) are famous comercial membrane use for the system and operate in the neutral pH values [9].
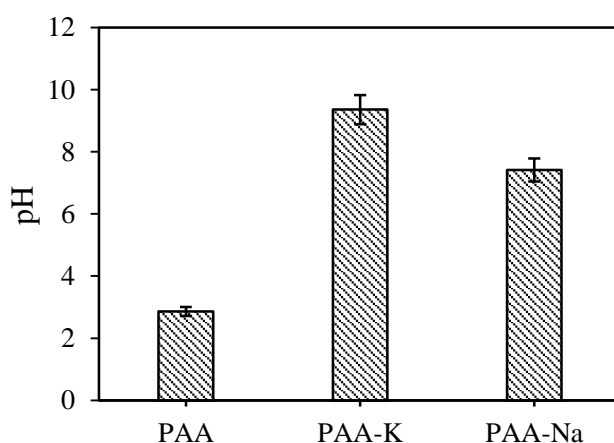

Figure 5 The pH of PAA, PAA-K, PAA-Na

3.1.3 Conductivity of PAA, PAA-K and PAA-Na

Figure 6 presents the conductivity of self-synthesized polyelectrolytes as draw solution in FO process. These were found that the conductivity were increased after salt co-polymerization.

PAA-Na showed the highest conductivity at 6.54 mS/cm while as the commercial presented at 5.3 mS/cm. These results are less than obtained by Huang *et al*. [12] at 47.5 mS/cm. These are difference value due to the initial moles are difference in mass concentration.
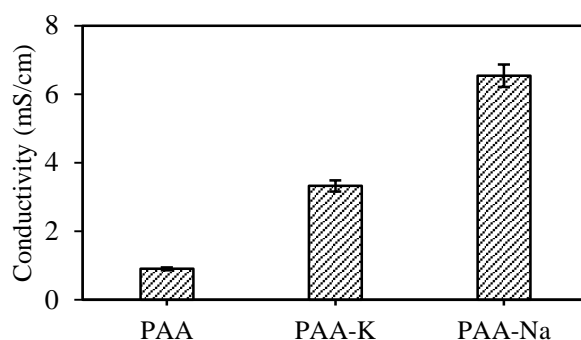

Figure 6 Conductivity of PAA, PAA-K, PAA-Na

3.1.4 Viscosity of PAA, PAA-K and PAA-Na

The viscosity of self-synthesized polyelectrolytes is presented in Figure 7. The viscosity increased from 21.48 257.79 226.28 mPa/s for PAA, PAA-K and PAA-Na, respectively. The viscosity of PAA-K shown higher with a larger of MW of draw solution. The viscosity of commercial PAA-Na is 0.1 mPa/s. It is higher solubility than the

self-synthesized PAA-Na. However, the higher of viscosity is the main problem in the FO process that decreased flux [12]. Nguyen *et al*. [10] said the hydrophobic of tail of surfactant show the reaction at the membrane surface that low RSF. These confirmed that behaviors because of the viscosity of self-synthesized polyelectrolytes is too high but less of RSF *(in section 3.2.1).*
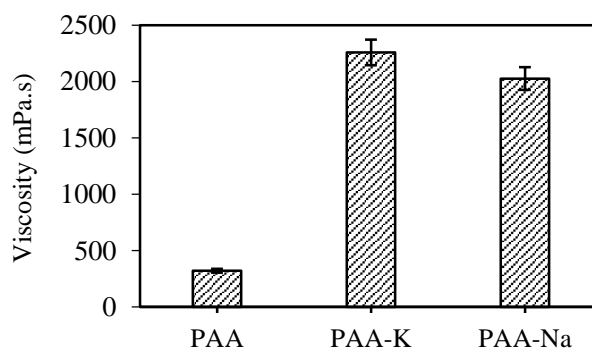

Figure 7 The viscosity of PAA, PAA-K, PAA-Na

3.1.5 Molecular Weight of PAA Salts and Their Osmolality

As the result, PAA salts in term of PAA-NA was lower molecular weight than PAA-K and PAA, respectively. In addition, it showed highest osmolality in this study (Figure 8). Table 1 presents the molecular weight of the PAA salts, the self-synthesized PAA-

Na is close to the commercial PAA-Na (MW1200). In comparison, self-synthesized polyelectrolytes is high osmotic pressure than the commercial PAA-Na. This results might be explained by the different concentration of the free counter ion in the solution from the synthesized process [11].

Table 1 The molecular weight of polyelectrolytes

Condition	m/z	Molecular (g/mol)
PAA	1,904	1,903
PAA-K	3,478	3,477
PAA-Na*	1,268	1,267
PAA-Na**	1,200	1,200

* Self-synthesized PAA-Na
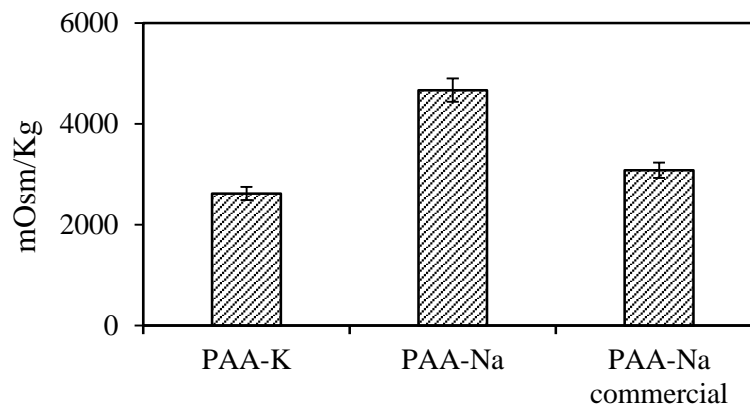** Commercial PAA-Na

Figure 8 The osmolality of PAA-K, PAA-Na and Commercial PAA-Na

3.2 FO performances

3.2.1 Water Permeation Flux and Reverse Solute Flux

The application of the self-synthesized PAA-Na and commercial PAA-Na as the draw solute in the FO system were evaluated by measuring the water permeation flux and reverse solute flux (RSF) values as shown in Figure 9. The water flux of the self-synthesized PAA-Na was higher than commercial PAA-Na due to their chemical

characteristics are difference especially the osmotic pressure. The osmorlity is the key parameters for the flux obtained. In addition, the molecular weight of polymer chains in the solution and the initial concentration are effect on the osmolarity. The RSF of both polyelectrolytes found that similar value at 0.023 and 0.024 gMH for self-synthesized PAA-Na and commercial PAA-Na, respectively. These result could be explained by the effect of the adding the surfactant that present hydrophobic interaction effect.

The hydrophobic tail of the surfactant interacts with the hydrophobic membrane and trapped the membrane pores, leading to a significant reduction in the reverse salt diffusion of Na^+ [10]. In addition, compared with the control by the NaCl was also investigated. The osmotic pressure of NaCl was high, but the salt conversion was also high.

Considering only the RSF, it was found that self-synthesized PAA-Na presented lower salt reversion than other. Moreover, the low RSF value due to the viscosity of PAA-Na is higher and molecular weight of PAA-Na is lower than others.
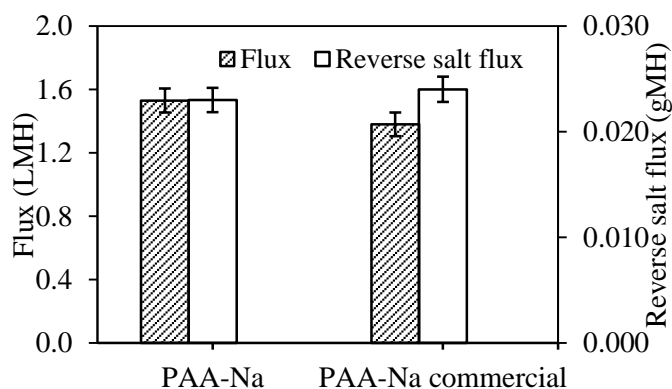

Figure 9 Water permeation flux and reverse solute flux of synthesis PAA-Na and Commercial PAA-Na

3.2.2   Draw Solution Recovery Process

Recovery process to achieve a constant concentration of draw solution by using Ultrafiltration system. The results was showed that the salt rejection were 54% and 21% for self-synthesized PAA-Na and commercial PAA-Na, respectively. In addition, self-synthesized PAA-Na is higher salt rejection because of higher molecular weight than commercial PAA-Na [12].

3.2.3 Stability of Synthesis PAA-Na

Figure 10 shows the stability values of the flux after fed through the Ultrafiltration process. It was found that the flux was gradually decreased for each recycle number. The decrease was synchronized with the research of Zhao *et al*. [14] that maybe the stability of the polymer in solution was loss due to the decrease of mas of polyelectrolytes.
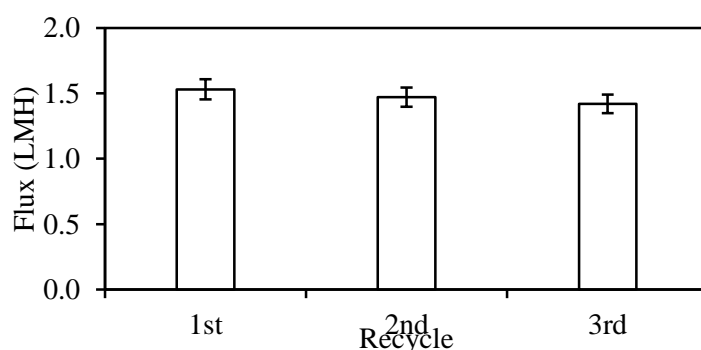

Figure 10 The recovery flux after filtrated by Ultrafiltration for each recycle

4.0 CONCLUSION

The self-synthesized polyelectrolytes of PAA-K and PAA-Na showed the increasing of hydrophilic functional group like carboxyl –OH or COOH. It was found that the lighter the molecular weight, the higher the osmolality and the greater the osmotic pressure. However, the molecular weight of PAA-Na was lower than PAA-K due to the different of the salt molecule compounds in salt polymerization. Self-synthesized polyelectrolytes obtained a small molecular weight and high osmotic pressure in the aqueous solution may exhibit a lower reverse solute flux in FO process. These result could be explained by the effect of the adding of the surfactant that presented hydrophobic interaction effect.

ACKNOWLEDGEMENT

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