

Properties of Zwitterionic Sulfobetaine Gels Containing Different Numbers of Methylene Units

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Abstract The present research was performed aiming to develop gel with the characteristic of reversible thermosensitive in adsorbing heavy metal ions from its solution. There were three gels used in this study to adsorb heavy metal ion from salt solution provided $Zn(NO_3)_2$; copolymer gel consisting of zwitterionic betaine *N,N*-dimethyl(acrylamidopropyl)ammonium propane sulfonate (DMAAPS), *N,N*-dimethyl(acrylamidopropyl)ammonium butane sulfonate (DMAABS), and DMAAPS copolymerized with thermosensitive *N*-isopropylacrylamide (NIPAM) gels. The aforementioned gels were employed to examine its ability in adsorbing and swelling after being synthesized through free radical polymerization before being affected by methylene spacer number, copolymerization, and temperature given. This research found that as the temperature increases, the ability of the gel in adsorbing the ions decreases. In the case of DMAAPS and DMAABS gel, the swelling degree value increases when the temperature also increases. Meanwhile, sulfobetaine which has larger spacer has higher adsorption ability but not with its swelling degree. In spite of having more spacer than DMAAPS, DMAABS found to have the smallest swelling degree value. In addition, NIPAM-co-DMAAPS was found to have both the highest adsorption ability and swelling degree value. Even though copolymer has less amount of sulfobetaine than DMAAPS and DMAABS gels, the copolymer gel was found to have higher ability of adsorption as many as ten times of other gels.

1 Introduction

The use of zwitterionic in polymer thermosensitive polymer copolymerization technique has become popular to be used as the alternative technique in several applications including biosensors, drug delivery system, catalysts, and separation media (Liu *et al.*, 2010; Ningrum, 2019). Research has been previously conducted aiming to remove Pb^{2+} from mixed solutions of Pb^{2+}/Cu^{2+} using zwitterionic hybrid polymer according to the polymerization reaction of ring-opening of pyromellitic dianhydride (PMDA) and sol-gel process by Liu *et al.* (Liu *et al.*, 2005). There are three types of zwitterionic polymer, including sulfobetaine, phosphobetaine and carboxybetaine which consist of both anionic and cationic groups. The anionic group includes sulfonate, phosphate and carboxylate, while the cationic group includes quaternary ammonium (Kudaibergenov *et al.*, 2006). The examples of zwitterionic sulfobetaine polymers are *N,N*-dimethyl(acrylamidopropyl)ammonium propane sulfonate (DMAAPS) and *N,N'*-dimethyl(acrylamide-propyl)ammonium butane sulfonate (DMAABS).

A previous study was conducted by Ningrum *et al.* (Ningrum *et al.*, 2015) aiming to investigate the relationship between ion ability in adsorption and swelling properties on sulfobetaine gel. When the gel polymer concentration was higher than 180 g/l and the swelling degree is low, no change was occurred at the amount of Zn^{2+} ions absorbed. Meanwhile, when the concentration was lower than 180 g/l and the s

welling degree was high, there is a decrease in the amount of Zn^{2+} ion absorbed. Meanwhile, the amount of Zn^{2+} ion adsorbed in the gel increased as $Zn(NO_3)_2$ concentration increases and the gels involved had the same swelling degree.

There are various previous researchers conducted aiming to investigate the copolymerization of sulfobetaine zwitterionic polymer and thermosensitive gel by several researchers. However, most of them only encouraged on the copolymer gel's synthesis and properties. The result of one of the previous research carried out by Ningrum *et al.* (Ningrum *et al.*, 2014) obtained the relationship between the swelling degree properties and DMAAPS gel in adsorbing ions in various solutions as well as how the concentration of the cross-linker affects the adsorption

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and the swelling of DMAAPS gel. The result obtained the relationship between the cross-linker concentration and DMAAPS gel adsorption ability in which the higher the cross-linker concentration, the better the DMAAPS gel in ion adsorption.

Thus, the purpose of this research was to investigate the spacer (methylene unit) amount within the sulfobetaine charged group in affecting the adsorption and swelling degree of the gel. Moreover, this research also aimed to know the comparison of the DMAAPS gel adsorption amount and copolymerization of DMAAPS with thermosensitive NIPAM at various cross-linker concentrations.

2 Experimental Section

This research used primary monomer in the form of N-isopropylacrylamide (NIPAM) obtained from KJ Chemicals Co., Ltd., Japan that has been purified through recrystallization using N-hexane. *N,N*-dimethyl-(acrylamidopropyl)ammonium propane sulfonate (DMAAPS) was synthesized through ring-opening reaction (Ningrum *et al.*, 2019) which was introduced by Lee and Tsai (Lee and Tsai, 1994). The reaction was carried out using *N,N*-dimethylaminopropylacrylamide (DMAPAA) obtained from KJ Chemicals Co., Ltd., Japan. and 1,3-propanesultone (PS) or 1,4-butanedisulfone (BS) obtained from Tokyo Chemical Industry Co., Ltd., Japan. Then, 100 g of DMAPAA and 200 g of acetonitrile was mixed and added by a dropwise of the mixture solution of PS or BS (75 g) and acetonitrile (75 g) for 90 minutes. The mixture of the solutions was then stirred at 30°C and then the stirring was continued for 16 h. After the stirring, DMAAPS or DMAABS crystal was then washed using 500 mL of acetone. After washed, the stirring was continued for 2 days at room temperature. After the stirring, white crystals formed which were then filtered and washed using 500 mL of acetone. Drying of the product was then performed using vacuum oven at the temperature of 50°C for 24 hours.

NIPAM-*co*-DMAAPS synthesis was carried out through free radical polymerization reaction. For the reaction, N-isopropylacrylamide (NIPAM), DMAAPS, *N,N'*-methylenebisacrylamide (MBAA) and *N,N,N',N'*-tetramethylethylenediamine (TEMED) were dissolved into distilled water until the volume of the total solution reaches 100 mL. The dissolved oxygen was removed through purging process in the solution using nitrogen gas for 10 minutes. A solution of 20 ml ammonium peroxodisulfate (APS) that has been purged previously was added to the monomer solution. The polymerization reaction occurred at 10°C for 6 h in flowing N₂ gas. The gel synthesis is described in the table as follows:

Table 1. Gel's Synthesis Condition

	Monomer	Concentration (mmol/L)
NIPAM- <i>co</i> -DMAAPS	NIPAM	800
	DMAAPS	200
DMAAPS	DMAAPS	500

DMAABS	DMAABS	500
Linker	MBAA	10, 30
Accelerator	TEMED	10
Initiator	APS	2

A separable four neck flask was used by placing a glass tube of 3 mm (ID) and 2 cm (L) in order to carry out the gel synthesis to obtain the cylinder gel. The polymerization reaction which results in the formation of the gel lasted for 6 h. The gels formed was then cut until the length becomes 3 mm. Distilled water was then used to wash the NIPAM-*co*-DMAAPS gel. After the washing, the gel was dried on Teflon paper spread on the petridish for several days. The petridish covered by plastic films with small holes aiming to reduce evaporation. The evaporation was reduced so that the drying process is slower and the gel does not crack. The other gels product was also made into small pieces, washed and dried using oven. After the drying, the gels were then mixed and the gels higher than 90 mesh size were chosen through sieving. There were two gels produced, cylinder gels used for the swelling test and the gels higher than 90 mesh size used for the gels adsorption tests. The concentration ions in the solution was obtained through Atomic Absorption Spectrophotometry (AAS) analysis.

2.1 Swelling degree test (SD)

The swelling degree (SD) test was conducted by letting the cylinder gels left for 12 h until it reached its equilibrium swelling. However, before and after reached the equilibrium swelling, its diameter was measured using millimeter block of 70°C. The solution temperatures for this study were 10°C, 30°C, 50°C, and 70°C. The following equation was used to calculate the swelling degree

$$Swelling\ Degree = \frac{d_{swell}^3}{d_{dry}^3} \dots\dots\dots 1$$

The d_{swell} shows the gel diameter when it reached equilibrium swelling at a certain temperature (diameter of swollen gel) while d_{dry} shows the dry gel diameter (dry gel).

2.2 Adsorption test

In the adsorption test, ZnNO₃ solution was used. In this case, 20 ml of ZnNO₃ solution in the desired concentration was added by one gram of copolymer gel. The mixing was placed in a glass bottle put into a waterbath and stirred for 12 h at the desired temperature in order to achieve equilibrium adsorption conditions. Centrifuge was used to separate the gel from the solution in order to calculate the concentration of cations and anions in the solution after the adsorption process. Then the gel was filtered with a syringe filter.

The following equation was used to calculate the amount ions adsorbed into the gel calculated from the concentration of cations and anions before and after the adsorption process,

$$Q = \frac{(C_0 - C)V}{m} \dots\dots\dots 2$$

The Q shows the number of cations or anions adsorbed or decanted, C_0 is the ions' concentration before the adsorption process in the solution, C is the ions' concentration after the adsorption process in the solution, while V is the volume of the solution and m is the dry gel weight (≥ 90 mesh). The ion concentration was determined using Atomic Absorption Spectrophotometry (AAS) analysis.

3 Result and Discussion

3.1. The Effect of Time on Gels' Adsorption Ability

The effect of the gel adsorption's time length on the amount of Zn^{2+} ions adsorbed in $Zn(NO_3)_2$ solution in the time range of 0-24 h is shown in Figure 1. From this figure, the time of NIPAM-co-DMAAPS gel in achieving its equilibrium adsorption in $Zn(NO_3)_2$ solution can be determined. In the first 6 h the amount of Zn^{2+} ions adsorbed increased significantly. However, later it showed a slight decrease in the next 6-12 h continued with a constant. The phenomenon is because a large concentration gradient between the copolymer gel in the first 6 h, so that the mass driving force before 6 h is greater than the driving force over 6 h. After the first 6 h, the ions adsorbed causing the concentration gradient decreases and the mass transfer rate becomes slower until finally reaches an equilibrium condition. The adsorption equilibrium achieved by the gel copolymers is above 12 h which will later be used in subsequent experiments (Ningrum *et al.*, 2015).

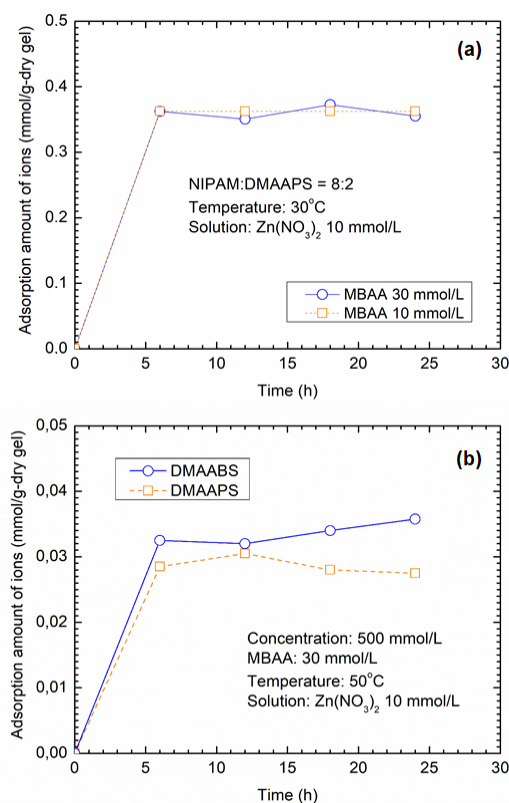


Figure 1. The effect of contact time on the adsorption ability of a) NIPAM-co-DMAAPS gels at

30°C.; b) DMAAPS and DMAABS gels at 50°C

3.2. The effect of temperature on gels adsorption ability

Effect of temperature on the adsorption ability copolymers gel is shown in Figure 2. In all gels, as the temperature increased, the gels' adsorption ability of the ions decreased. The increase of the temperature was caused the bond between the ion and the charged group in the gel (N^+ and SO_3^-) weak so that the bond in the gel was dominated by intra-group, inter-chain, and intra-chain bonds. The number of ions adsorbed by DMAAPS gel (3 methylene spacer) increased with cross-linker concentration. The reason was due to in the gel having higher cross-linker concentration the bond formed was denser. This limits the gels' ability to expand and shrink. When the gel expands, the gel's swelling ability was limited by the bond formed from the polymer and cross-linker so that the distance between the charged groups was closer. Meanwhile, if the cross-linker concentration was low, the gel can expand better so that the distance between the charged groups was getting bigger. The distance between charged groups that are increasingly close together made it easier for intra-group bond (Ningrum *et al.*, 2017a).

Ion adsorption on DMAABS gel (4 methylene spacer) is shown in Figure 2(b). In the figure, it can be seen that DMAABS gel adsorption ability was higher than the DMAAPS gel adsorption ability. This is in accordance with the initial hypothesis that further distance between the charged groups make the bonds between the charged groups weaker and cause the interaction within the gel between the solution ions and charged groups increased. There was no difference between the cross-linker gels with low and high concentration due to DMAABS properties which has hydrophobic properties (Ning *et al.*, 2013b). Since the gel was more hydrophobic, the permeability of the gel was low so the solution was difficult to penetrate into the gel. The bonding between the charges in the gel with longer methylene spacers did not affect the flexibility of the charged group (Weers *et al.*, 1991). Carboxybetaine molecule with methylene spacer molecules less than 3 between its charged groups have lower pK_a compared to the molecule which has more than 3 methylene spacer. This indicates that carboxybetaine with methylene spacer <3 has a weak ability to interact with water compared to the carboxybetaine which has methylene spacer >3 . In addition, between two charged groups in 1 molecule zwitterion separated by methylene spacer >4 did not affect each other with one another while in zwitterion, the charged groups are separated by methylene spacers <3 , charged groups on the same molecule that are more interactive affect each other (Shao and Jiang, 2013). Looking at the similarities of sulfobetaine and carboxybetaine, it can be approximated that sulfobetaine with methylene spacer >3 (in this case DMAABS) is easier to bind to water so that it inhibited $Zn(NO_3)_2$ ions binding to charged groups (N^+ and SO_3^-). Poly (DMAABS) itself had an effective inter-chain pair

formation in charged groups inside sulfobetaine. Because the inter-chain bonds occurred were very strong, the difference in cross-linker did not have any significant effect on gels' ion adsorption (Ning *et al.*, 2013a).

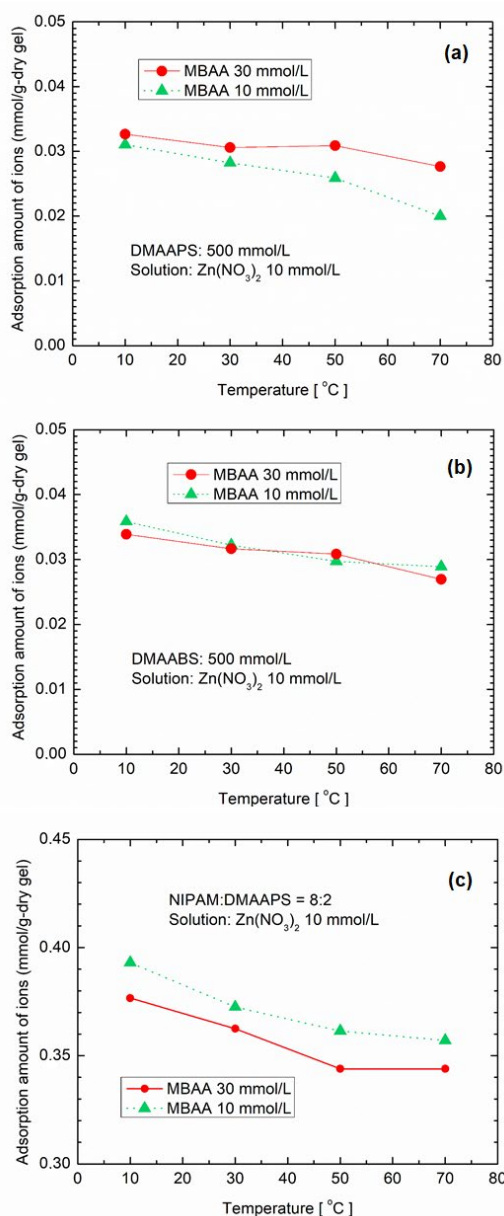


Figure 2. Effect of temperature on the adsorption ability of a) DMAAPS, b) DMAABS, and c) NIPAM-co-DMAAPS gels

Temperature also affected the ions' adsorption ability, in which the more increase the temperature, the weaker the interaction of ions in the solution and the group of charged groups. In the case NIPAM-co-DMAAPS, the copolymerization DMAAPS with thermosensitive NIPAM increased the gels' adsorption ability ten times as seen in Figure 2(c). The increase in adsorption ability was affected by the presence of NIPAM which acts as the separator between DMAAPS molecules. NIPAM is a thermosensitive polymer well at low temperatures (Ningrum *et al.*, 2017b). When NIPAM expanded, the distance between DMAAPS molecules increased and the intra-chain, inter-chain and intra-group

bonds decreased. With the decrease of the bond, the charged groups can bind ions in the solution. According to the figure above, it can be obtained that when there was an increase in the temperature, the gel adsorption ability decreases. At high temperatures, the adsorption ability of the gel was low, this was due to an increase in temperature which causes the interaction between solution ions and charged groups in the gel weaker. In addition, the reduced ability of the gel to adsorb ions was caused by gels that shrink at high temperatures so that the gel became denser. When shrink, the ions were pushed out from the gel because of the inter-chain, intra-chain, and intra-group bonds. In addition, thermal motion can also weaken the strength of inter ion bonds (Ningrum *et al.*, 2014).

3.3 The Effect of Temperature on Swelling Degree

Figure 3 shows the effect of temperature on the gel's swelling degree. For DMAAPS and DMAABS, the gels' swelling degree increased as the temperature increased. However, when the temperature increased, the NIPAM-co-DMAAPS gel's swelling degree decreased. This is because NIPAM concentration was higher than DMAAPS so that the nature of the copolymer gel was dominated by NIPAM property. The higher the concentration of the cross-linker, the gel swelling degree decreased, as seen in the DMAAPS gel and NIPAM-co-DMAAPS gel. The high cross-linker concentration caused the gel stiff. Because the polymer is in the form of a gel, when the chain expanded, the entire bond swells. However, because of the higher cross-linker, there is a limitation on the gel's swelling ability. The cross-linker concentration has no significant effect in DMAABS gel. This is because the bonds between molecules are strong and the number of inter-chain bonds present in DMAAPS is high so that the polymer chain entangle (Ning *et al.*, 2013a).

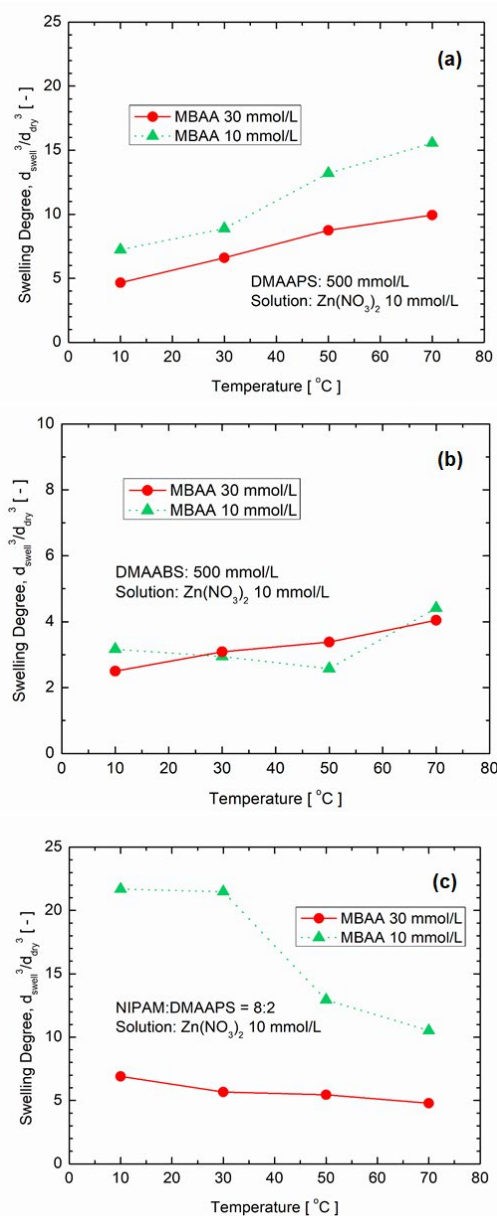


Figure 3. The Effect of temperature on the swelling degree of a) DMAAABS, b) DMAAPS, and c) NIPAM-co-DMAAPS gels

4 Conclusion

The equilibrium adsorption of the sulfobetaine gel and its copolymerization with NIPAM was achieved above 6 h. The cross-linker has a significant effect on swelling degree of the DMAAAPS and NIPAM-co-DMAAPS gels where the addition of the cross-linker concentration decreases the swelling degree value. However, in DMAAABS gel, the addition of cross-linker did not have any significant effect on the swelling degree value. The ability of NIPAM-co-DMAAPS adsorption increased by the decrease of the cross-linker's concentration, while in DMAAAPS and DMAAABS the change in cross-linker concentration did not have any significant effect on the gel adsorption ability. NIPAM-co-DMAAPS gel had the highest adsorption value which was then followed by DMAAABS gel and the lowest was DMAAAPS gel. The

adsorption ability of the gel both NIPAM-co-DMAAAPS, DMAAAPS, and DMAAABS decreased as the temperature increases as well. In the case of swelling degree, NIPAM-co-DMAAAPS has the highest swelling degree followed by DMAAAPS and the lowest was DMAAABS. As the temperature increased, the NIPAM-co-DMAAAPS gel's swelling degree also decreased. Meanwhile, as for the DMAAABS and DMAAAPS gel, their swelling degree increased as the temperature increased.

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