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APPLICATION OF POLY (SODIUM ASPARTATE) SYNTHESISED UNDER MICROWAVE RADIATION IN WATER SOFTENING

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ABSTRACT

Hard water used in households and industrial plants generates many problems due to calcium and magnesium ions abundance. Their presence leads to scale formation in water pipes and all elements that contact with water. Therefore pipes clogging and damage of an equipment can appear. Bivalent ions can be eliminated by various methods. The most popular include chemical precipitation, ion-exchange resin or zeolite treatment and different electro membrane systems. Unfortunately, they have one major disadvantage – high price and very often are difficult to apply. Novel materials for metal ions adsorption should be not only cheap and effective but also environmentally friendly. Therefore new synthesis methods must be developed which would meet Green Chemistry principles. Poly (succinimide) and its derivatives are known of being not only non-toxic but also easily biodegradable and are capable of ion chelation. Sodium salts of poly (aspartic acid) possess ability of binding calcium and magnesium ions thanks to the carboxylic group presence in their structure. They can be easily obtained via PSI basic hydrolysis. In this paper a novel microwave-assisted poly (succinimide) synthesis method is proposed. Moreover, chelating capability of poly (sodium aspartate) was investigated by two different methods and chelating capacity was determined.

INTRODUCTION

Water purification for domestic and industrial purposes has been applied for many years. Beyond different contaminants that have to be removed, a big problem are metal ions such as Ca^{2+} and Mg^{2+}. Their presence has not only negative impact on cleaning agent's efficiency but also causes scale formation. This can lead to many failures in boilers, dishwashers, washing machines or heat exchangers [1-3]. Scale accumulation can cause clogging or even damage of water pipelines in many industrial settings. Therefore deterioration of equipment working quality occurs. Many commercial methods of water softening are known, but very often they are not only expensive but also have negative impact on the environment. The most popular methods include chemical precipitation, ion-exchange resin or zeolite treatment. Also electro membrane systems are used like electro dialysis or electro dialysis reversal. Moreover, very often for the metal ions removal Nano filtration and reverse osmosis is applied. Currently the world is facing big problem with ongoing pollution of the environment. Therefore all methods for water treatment should be not only inexpensive, easy in use and easily accessible but also eco-friendly. For this reason new ways for abundant divalent metal ions must be developed. To create innovative anti-scale agent their environmental impact must be taken under consideration. Thus potential materials obtained for metal ions adsorption should be synthesized meeting Green Chemistry principles [4-6].

Poly (succinimide) (PSI) is a polymer known of its biodegradability and biocompability. Since it is non-toxic and has ant scale properties, this compound and its derivatives are increasingly used for water treatment instead of hazardous poly (acrylates). Sodium salts of poly (aspartic acid) (PASANa) due to the carboxyl group presence are capable of bivalent ions chelation. Thus PASANa can successfully bind Ca^{2+} and Mg^{2+} significantly reducing calcium carbonate formation without having any negative impact on the drinking water properties. They can be obtained directly from PSI by basic hydrolysis during which imide rings opening occurs. Poly (aspartic acid) and poly (succinimide) synthesized from L-aspartic acid are expensive materials, therefore an alternative method of PASANa obtainment must be applied. Microwave-assisted synthesis generates possibility of PSI obtainment with reduced amount of solvents used and decreased reaction time, therefore meeting Green Chemistry principles [7-13].

In this article chelating studies of poly (sodium aspartate) obtained from poly (succinimide) are presented. For PSI synthesis microwave protocol was applied and alternative substrates were used. An average molecular weights of the obtained product was determined using GPC method. Calcium ions adsorption was investigated by mixing Ca^{2+} ions solution of known concentration with an appropriate amount of PASANa solution. Calcium ions concentrations in ready mixtures were measured after 0, 1, 24, 48, 72 and 144 hours. Also foam tests for water softening activity investigation were performed. Basing on the obtained results also poly (sodium aspartate) chelation capacity was calculated.

MATERIALS AND METHODS

Materials

Maleic anhydride and urea (analytic grade) used for PSI synthesis, buffer solutions, sodium hydroxide and 0.02M EDTA solution (analytic grade) for basic hydrolysis and chelating process investigation were supplied from POCh Gliwice (Poland).

Methods

All syntheses were carried out using Milestone START Labstation microwave reactor of maximum power 1000 W with magnetic stirrer and optical temperature sensor.

Poly(succinimide) synthesis

For the poly(succinimide) obtainment an appropriate amount of maleic anhydride and urea were placed in a reacting vessel and 5 ml of distilled water was added. Then reacting program was set and switched on. As a product pink-brown powder was achieved.

Average molecular weight determination

Average molecular weight was determined using Gel Permeation Chromatography method. In this research GPC chromatograph Knauer SMARTLINE was used. The system was equipped with Smartline 1000 pump with maximal flow of 10 ml/min, degassing system Manager 5000, thermostat Smartline 4000 and refractive detector Smartline 2300. A column PolySep GFC P4000 was used.

PSI sample hydrolysis

To prepare chelating agent solution 0.500 g of the synthetized PSI sample was added to 25 ml of distilled water. The suspension was magnetically stirred. Then 2 ml of 10 % sodium hydroxide solution was added. The color of the mixture changed from pink to deeply red and became fully transparent after 24h. The hydrolysis reaction occurs not only in strongly alkaline solution but also in moderate conditions. In the Figure 1 it can be noticed that pH of the reacting mixture was deceasing strongly after first portion of NaOH solution addition. During hydrolysis reaction the decrease of pH was lower till any change was observed after next addition. The ready chelating solutions contained poly(sodium aspartate) and an excess of unreacted sodium hydroxide. The mixture was transferred to100 ml volumetric flask and distilled water was added to up to marked line. The results of PSI hydrolysis are presented in the Figure 1.

Calcium ion and titrating solutions preparation

To prepare calcium ion solution that would simulate hard water, 2.148 of gypsum ($CaSO_4 \cdot 2H_2O$) was dissolved in 500 ml of pure distilled water. The concentration of calcium ions was 0.0125 M (0.500 g/L). Dissolution of calcium sulfate is known to be a long gradual process, therefore the mixture had to be mixed and left overnight. Standard 0.02 M EDTA solution was prepared by dissolving 7.445 g of EDTA disodium salt.

Chelating process investigation

Standardization of calcium ion solution and calibration of the automatic titration system.

To measure calcium ion concentration in prepared gypsum solution, potentiometric titration was applied. The titrating layout consisted of high quality universal electrochemical ELMETRON CX-551 millivoltmeter allowing to collect data automatically in a computer. Medical syringe pump was adopted to potentiometric titrations and the flow of titrant was carefully estimated. The speed of titration was 0.4520 ml/min of 0.02 M EDTA standard solution. To determine calcium ion concentration 1 ml of the sample was transferred to the beaker and 14 ml of distilled water was added to fully dip the combined calcium electrode. The sample was titrated with speed of 0.4520 ml/min 0.02 M EDTA. The standardization and verification of the correctness of titrating system was done by second titration. The titration curves are presented in the Figure 2.

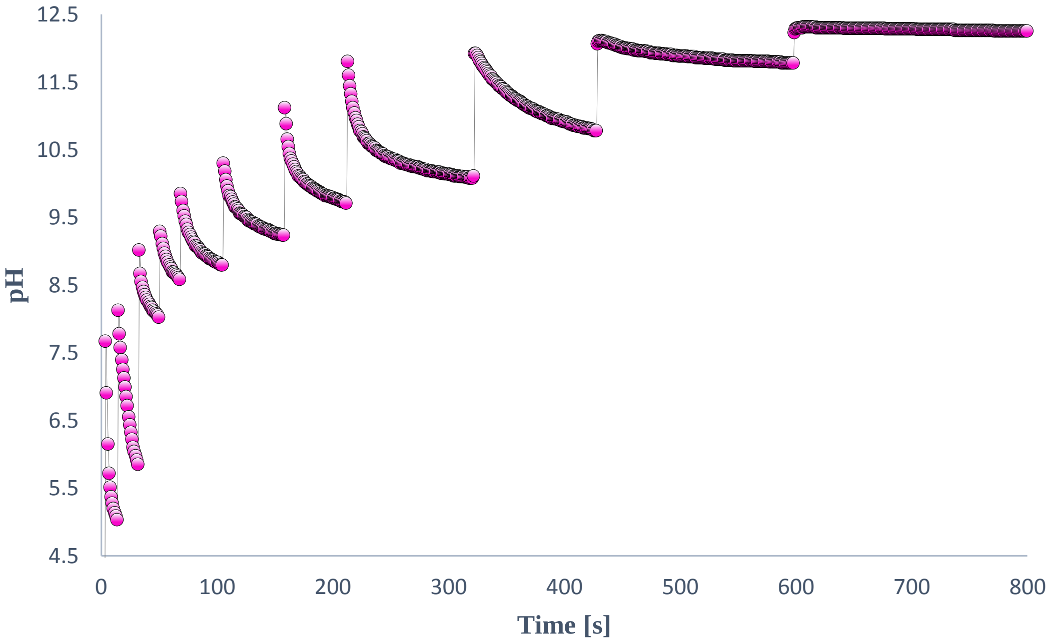

Figure 1. pH change during addition of fresh 0.1 and 0.2 ml portion of 10 % NaOH solution in time to 0.5 g of PSI water suspension (40 ml H_2O)

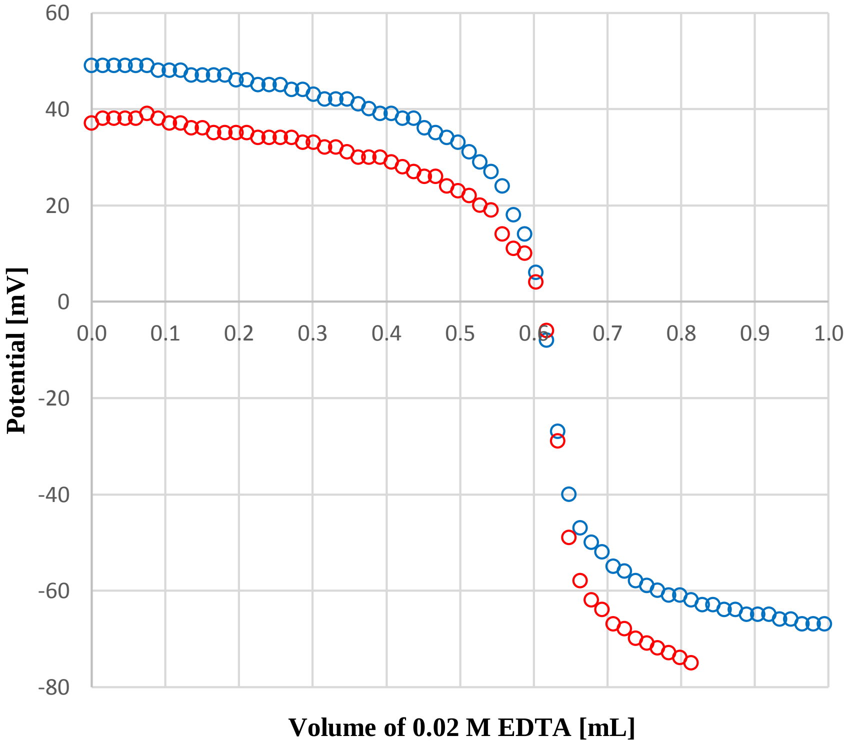

Figure 2. Titration curves of 1 ml of calcium ion solution prepared by dissolving 2.148 g of gypsum in 500 ml of distilled water

The concentration of calcium ions was 0.01052 M. Before chelating measurements calcium ion selective electrode was calibrated. The standard calcium ions solutions were prepared by diluting 0.01252 M solution of $CaSO_4$. To all samples 0.1 ml 10 % NaOH solution was added to compensate the ion strength and minimize the difference between standard solutions and mixtures of Ca^{2+}/poly(sodium aspartate) samples. The calibration equation for calcium ion selective electrode was:

$$EMF = 11{,}292 * \ln(c_{Ca^{2+}}) + 129{,}04$$

$$c_{Ca^{2+}} = e^{\frac{EMF-129{,}04}{11{,}292}}$$

Measurement of the poly(sodium aspartate) chelating capacity

Three samples of hydrolyzed PSI were prepared. To 10 ml of poly(sodium aspartate) 10, 20 and 30 ml of 0.01252 M $CaSO_4$ solution were added respectively. The solutions were mixed and potentiometrically titrated with a constant titrant flow rate after 1, 24, 48, 72, and 144 hours. Additionally samples containing the same concentration of calcium ions without poly(sodium aspartate) were titrated to compare the change of free calcium ion concentration in investigated solutions. The titration curves are shown in the Figures 3,4 and 5.

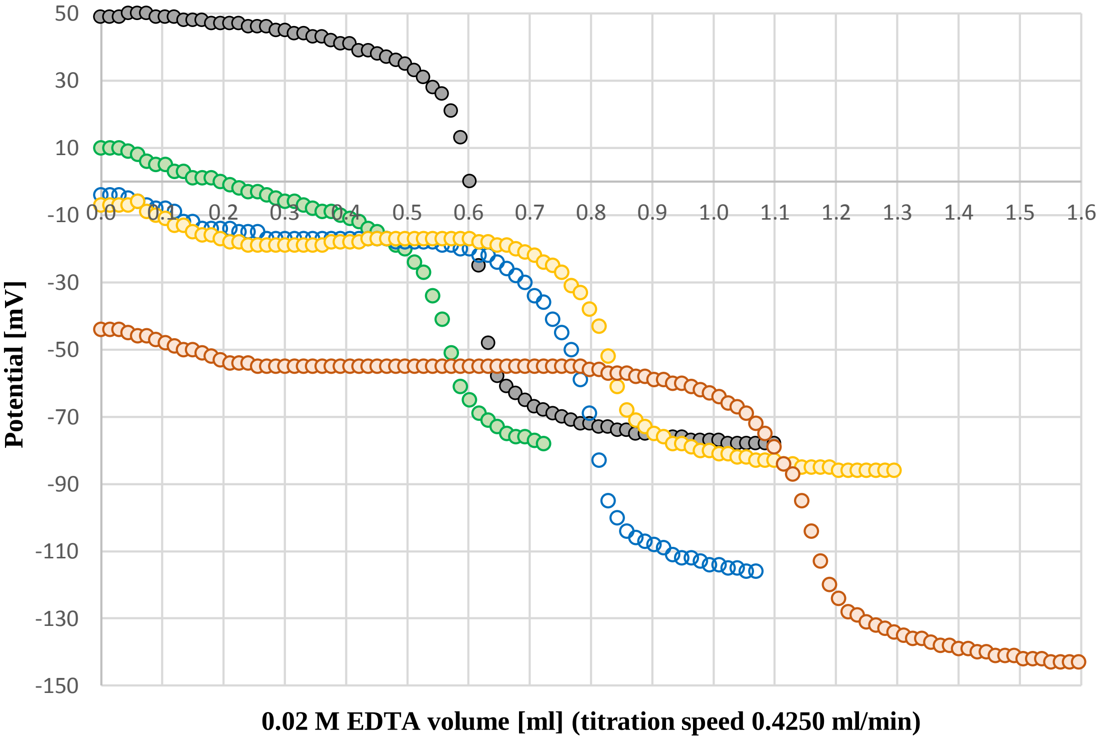

Figure 3. Titration curves of 2 ml of chelating mixture consisting of 10 ml of PASANa and 10 ml of 0.01252M $CaSO_4$ solution (--- blank solution, --- after 1 hour, --- after 24 hours, --- after 48 hours and --- after 72 hours)

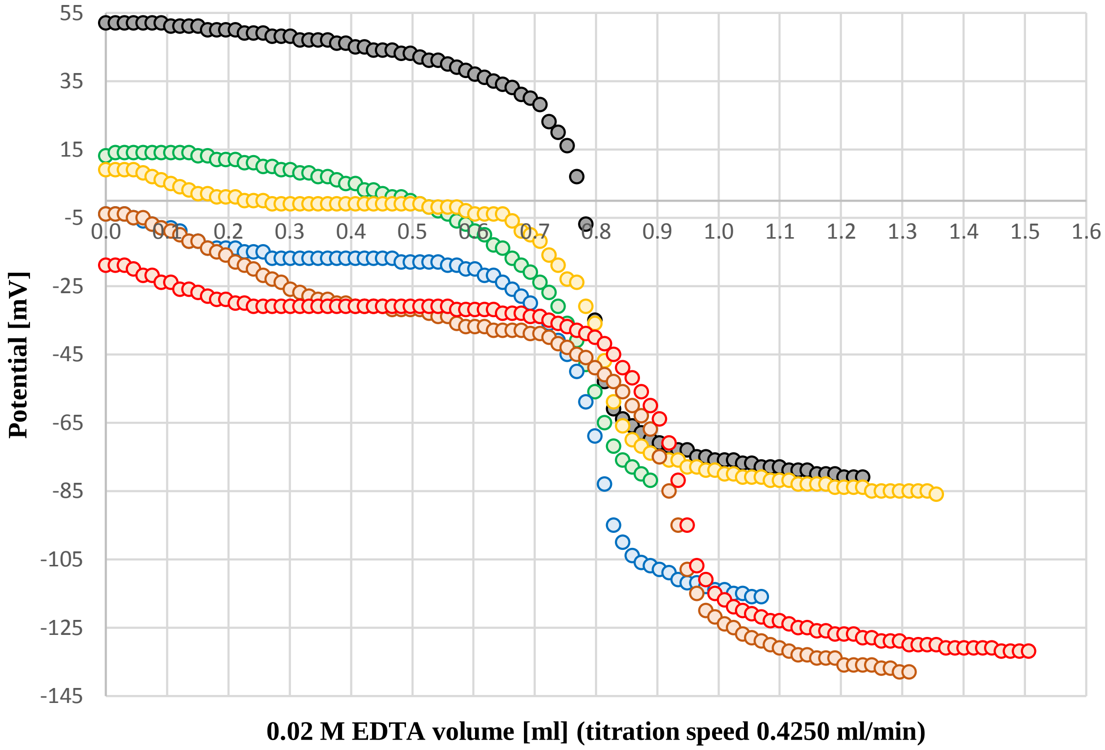

Figure 4. Titration curves of 2 ml of chelating mixture consisting of 10 ml of PASANa and 10 ml of 0.01252M $CaSO_4$ solution (--- blank solution, --- after 1 hour, --- after 24 hours, --- after 48 hours, --- after 72 hours and --- after 144 hours)

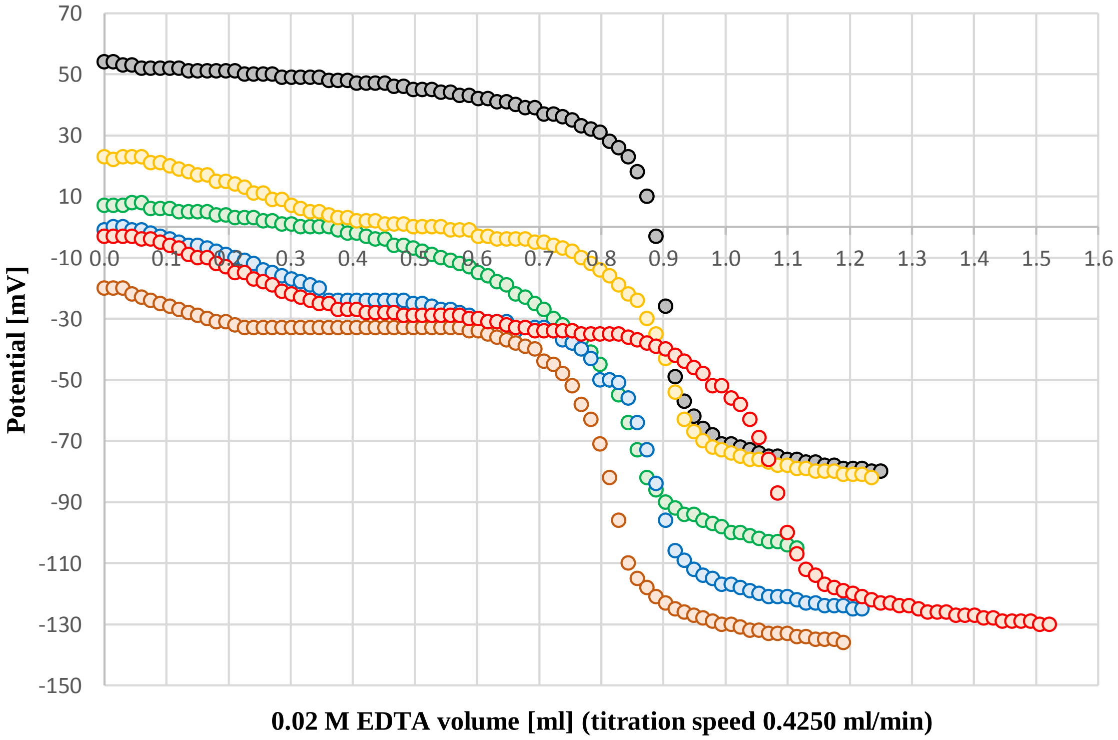

Figure 5. Titration curves of 2 ml of chelating mixture consisting of 10 ml of PASANa and 10 ml of 0.01252M $CaSO_4$ solution (--- blank solution, --- after 1 hour, --- after 24 hours, --- after 48 hours, --- after 72 hours and --- after 144 hours)

Foaming test

To confirm the chelating properties and utility of poly(sodium aspartate) water solutions as a water hardness leveler, foaming test was carried out. A solution of potassium soap in distilled water was prepared. The concentration of potassium soap in water was 0.2 %. A 0.1, 0.25, 0.5, 0.75, 1, 2, 5, 10, 20 and 35 ml of poly(sodium aspartate) and 100 ml of tap water were mixed and the solution was left for 4 hours to complex calcium ions. After that time samples of the mixture were taken to analysis. To a test volume of tap water and poly(sodium aspartate) mixture, soap solution was gradually added from burette. After adding 1 ml of soap solution, the tube was vigorously shaken and foam formation was observed. The addition of soap solution was stopped when the foam after shaking had 3 cm height and was stable for 30 seconds.

RESULTS AND DISCUSSION

Poly(succinimide) synthesis under microwave radiation was rapid and efficient. During the polycondensation reaction water was easily distilled and pink product was received. Proposed synthesis method enabled power and chemicals consumption reduction. Therefore, this obtainment pathway can be a cheaper alternative for other synthesis methods. PSI easily hydrolyses in basic solutions and dark orange – red solution was received. The average molecular weight determined using GPC method was in range between 20 000 to 40 000 g/mol. An impact of average molecular weight value on hydrolysis process was observed. The lower it was the quicker process occurred since ion binding functional groups were more accessible for calcium ions.

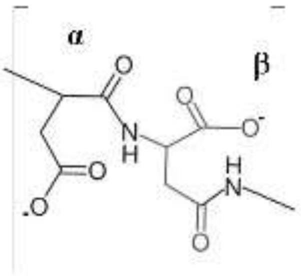

Figure 6. Chemical structure of poly(sodium aspartate)

Structure of the obtained poly(sodium aspartate) is presented in the Figure 6. It can be noticed, that PSI consists of two units: α and β. Hydrolyzed PSI is water soluble because carboxylic groups are dissociated and strongly interact with water molecules. Thanks to close presence of dissociated carboxylic group and amide groups, poly(sodium aspartate) exhibit chelating properties. It was confirmed that PASANa has good calcium ions chelating properties. From the titration curves it can be observed that the amount of free calcium ions decreases rapidly during the first hour after hydrolyzed product addition. The concentration of Ca^{2+} ions decreases gradually during first week and a state of equilibrium after that time is reached. The usage of murexide as an indicator of end point of titration would be very doubtful, because complexometric indicator may change color in different time during titration. Calcium ion selective electrode is a better indicator of reactions and equlibria changed in the solution. During titration of samples after 74 and 144 hours it could clearly be noticed that the potential of the electrode decreases because free calcium ion are chelated by EDTA. After that a new equilibrium state appears. Calcium ions were removed from poly(sodium aspartate) and bonded with EDTA. The potential didn't change during titration with constant flow rate. When polymer lost calcium ions, potential drooped to a very low negative values that indicated the amount of free calcium ion was extremely low. The interesting fact was the change of the end point of titration. The amount of calcium in solution was the same but the end point of titration changed. It was related to slow speed of calcium ion exchange from polymer to a solution during titration. The end point of all mixtures was the highest for the oldest samples what means that calcium ion bonding force increased during time. This phenomenon may be also connected with the fact that after 1 - 3 days the mixture became dull and the calcium salt of poly(aspartic acid) precipitated.

Table 1. The concentration change of free calcium ions in time

The ratio of solution volumes Polymer : Ca^{2+}	Free Ca^{2+} ions concentration [mg/L]			
	0 h	1 h	24 h	144 h
1 : 1	250	8	2	0,02 (74h)

1 : 2	326	10	2	0,6
1 : 3	390	6	4	0,6

Foaming test was applied to investigate the practical use of prepared chelating agent solutions. The amounts of reagents are presented in Table 2.

Table 2. The foaming test - amounts of reagents

Amount of PASANa solution [ml]	Tap water [ml]	Amount of mixture taken to analysis [ml]	Amount of soap solution necessary to form stable foam [ml]	Calculated amount of PASANa added to one liter of tested hard water [g]
0,00	100 (distilled)	10,0	1,2	0,00
0,00	100	10,0	12,0	0,00
0,25	100	10,0	11,5	0,01
0,50	100	10,0	11,5	0,03
0,75	100	10,1	11,5	0,04
1,0	100	10,1	11,5	0,05
2,0	100	10,2	11,5	0,10
5.0	100	10.5	10.0	0.25
10.0	100	11.0	10.0	0.50
20.0	100	12.0	6.0	1.00
35.0	100	13.5	1.0	1.75

During addition of soap solution to all samples, white fluffs were forming in a considerable quantity, but the solution was transparent. After shaking and adding more soap solution to graduated test tubes, the fluff began to destroy and a mixture of high turbidity was created. It can be noticed that to create foam in 10 ml of distilled water 1.2 ml of 2 g/L soap solution was necessary. The highest amount of soap was required to form stable soap in pure tap water. The soap consumption was ten times higher than in distilled water. 1.75 g of PASANa was enough to achieve identical foaming properties that distilled water has.

CONCLUSION

Microwave-assisted synthesis enabled poly(succinimide) obtainment characterized by good physicochemical properties, average molecular weight and meeting Green Chemistry principles. Quite low average molecular weight of the obtained polymer has a significant impact on the hydrolysis speed. Basic hydrolysis resulted in poly(sodium aspartate) formation which was further used for its chelating ability studies. Both foam tests and Ca^{2+} ions concentration changes in time after PASANa addition demonstrate that this innovative biodegradable polymer can be considered as an effective and easy in use eco-friendly anti-scaling agent.

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