Equilibrium Swelling Study of Cationic Acrylamide-Based Hydrogels: Effect of Synthesis Parameters, and Phase Transition in Polyelectrolyte Solutions

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Abstract

Cationic copolymer gels of acrylamide and [(methacrylamido) Propyl] trimethyl ammonium chloride (MAPTAC) were synthesized by free radical aqueous solution polymerization. The Taguchi method, a robust experimental design, was employed for the optimization of the synthesis based on the equilibrium swelling capacity of the hydrogels. Based on Taguchi method a standard L_{16} orthogonal array with five factors at four levels was designed and experiments were done in accordance with it. The effects of network composition such as cross-linker density, ionizable monomer and total monomer concentration together with the initiator concentration on the equilibrium swelling capacity of hydrogels in distilled water were studied. From the analysis of variance (ANOVA) of the test results, the most effective factor controlling equilibrium swelling capacity was obtained and maximum water absorbency of the optimized hydrogel was found to be 3570 g/g. The presence of counterions in the external solution suppressed swelling of optimized hydrogel and this effect was pronounced with bivalent counterions. By using the thermodynamic model, the experimental data were analyzed and the cross-linking efficiency for the polymerization reaction was calculated to be about 40%.

Keywords: Acrylamide, Cationic, Hydrogel, Swelling, Taguchi

Introduction

Polymeric gels are 3-Dimensional cross-linked networks and are able to absorb a high amount of their surrounding solvents. These networks act as a filter and let some of the solvent's molecules pass through it freely, while the matrix network of the gel keeps the liquid within [1]. This polymeric network is called hydrogel when the surrounding solution is water. Hydrogels are able to absorb a considerable amount of water due to their hydrophilic characteristics [2]. That is why they have wide spread applications in bio-engineering, drug delivery [3] and release control [4], gel actuators, contact lenses, enzymes immobilization, agricultural and tissue industries [5, 6].

Ionized hydrogels (polyelectrolyte gels) have become very important due to their high mechanical properties and their great ability to absorb water and ion [7]. Obviously, in addition to the environmental conditions such as temperature, ionic strength, pH, etc in which gels are grown, the conditions in which gels are synthesized such as the initial concentration of monomers, the amount of cross-linking agent and the synthesis temperature are effective on the structural properties and swelling behaviour of the gels. Various studies have been carried out on the effect of the abovementioned parameters on the structure of the hydrogels, especially the effect of initial concentration of monomers [8, 9], the amount of the cross-linking agent [10, 12], and the dissociated co-monomer [7, 11, 23].

The effect of temperature and the amount of initiator on the structure and the swelling behaviour of these gels are not known clearly yet. The effect of the simultaneous changes in all of the said parameters on the structure and swelling behavior of the hydrogels has not yet been studied either.

The objective of this work is to study the effects of the simultaneous changes in 5

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parameters on the final amount of hydrogel swelling. The 5 varying parameters in this study are the initial concentration of monomers, the molar ratio of cross-linking agent, the amount of dissociable monomer, the reaction temperature, and the amount of the initiator of the reaction. Synthesizing a hydrogel able to absorb plenty of water and ion in addition to suitable mechanical properties is one of the other objectives of this work. These kinds of hydrogels are favored in agricultural industries, heavy metal elimination, and solvents recovery processes [5, 13].

This work is divided into three parts. In the first part, the effect of simultaneous changes in the said 5 parameters on the final amount of swelling was studied by using Taguchi method. This method can be used to optimize variables affecting free swelling capacity of cationic superabsorbent hydrogels [14]. The selection of the parameters was done based on our pervious practical experiments in this area. After performing the experiments, results were analyzed through the analysis of the variance (ANOVA) to determine the partial contribution of each factor and the optimum conditions. In addition, one can verify the optimal design parameters through confirmation experiment. In the second part, an optimised hydrogel with proper swelling and mechanical properties was chosen, based on the results of the first part, and its phase transformation in various electrolyte solutions such as NaCl, $CaCl_2$, and Na_2SO_4 was studied. These solutions had an ionic strength ranging from 10^{-5} to 1 M. In the third part, the represented thermodynamic model based on theories of Florry-Rehner was compared with the experimental data and some network parameters such as $\overline{M}_C$ and χ were calculated.

1- Theory

Swelling occurs when there is a positive osmotic pressure difference (driving force) between the hydrogel network and the surrounding solution. According to Prausnitz et al model [17], $\Delta\Pi_{swelling}$ consists of three different contributions: $\Delta\Pi_{mixing}$, $\Delta\Pi_{elastic}$, and $\Delta\Pi_{ion}$. This model is based on theories of Flory and Rehner, indicating that the elasticity and mixing contributions are totally independent and can be added linearly. These forced all together constitute the driving force of the swelling. The process of gel swelling will end when the sum total of these forced equals zero (equilibrium state).

$$\Delta\Pi_{swelling} = \Delta\Pi_{mixing} + \Delta\Pi_{el} + \Delta\Pi_{ion} = 0 \quad (1)$$

These portions shall be analyzed hereafter.

1-1- Osmotic Pressure of Mixing

In order to calculate the osmotic pressure of mixing according to Florry-Rehner theory, the hydrogel is assumed to be chains of uncross-linked polymers with similar concentrations. The chemical potential difference caused by the mixing of polymer can be explained by Florry-Huggins theory in which all interactions between the solvent molecules and polymer chains are random. Florry-Huggins model [18] can be used to calculate the chemical potential difference of mixing as follows:

$$\Delta\Pi_{mixing} = -\frac{\Delta\mu_{mixing}^{FH}}{V_1} = -\frac{RT}{V_1}\left(\ln(1-\varphi_2) + \varphi_2 + \chi\varphi_2^2\right) \quad (2)$$

χ is Flory parameter that characterizes the polymer solvent interaction energy.

1-2- Elastic Energy Caused by Deformation of the Network

There are two theories, affine and phantom, to explain the elastic behaviour of the network [20]. According to affine model, the fluctuations of the joints are heavily affected by the neighbouring chains. However, such suppressions have been ignored in phantom model and the fluctuations of the joints are assumed to be free. The real behaviour of the network falls between these two extremes, but the network behaviour can be well explained by phantom theory for the networks which swell considerably [16]. If Gaussian statistics are employed to explain the chains behaviour, the osmotic pressure difference caused by the deformation of the network can be calculated by the following equation.

$$\Delta\Pi_{elastic} == -\frac{\Delta\mu_{elastic}^{Phantom}}{V_1} = -\left(1-\frac{2}{\Phi}\right)\frac{RT\rho_2}{\overline{M}_C^{eff}}\varphi_2^{1/3} \qquad (3)$$

1.3. Ionic Osmotic Pressure Difference

The fixed charges on the network chains due to the presence of MAPTAC monomers in the network chains result in an asymmetric distribution of the ions inside and outside the hydrogel and its surrounding electrolyte solution. Such asymmetric distribution is the key factor in the creation of ionic osmotic pressure difference, which is added to other contributions as ions contribution. According to ideal theory of Donnan, the osmotic pressure caused by ions is defined as follows:

$$\Delta\Pi_{ion} = RT\sum_i \left(C_i^{gel} - C_i^{solution}\right) \qquad (4)$$

The chemical potential of the ions inside and outside the hydrogel must be equal in the equilibrium state. If the average activity coefficient of the ions inside and outside the network are presumed to be a little deviated from the ideal state, then the following equation can be used for the equilibrium state of the solution according to Donnan's equilibrium theory.

$$\left(C_{cat}^{gel}\right)\left(C_{an}^{gel}\right) = \left(C_s^{Solution}\right)^2 \qquad (5)$$

Considering the electroneutrality inside the hydrogel, the following equation can be written.

$$C_{cat}^{gel} + IC_{mc}\frac{\varphi_2}{\varphi_{2c}} = C_{an}^{gel} \qquad (6)$$

I is the fraction of the monomers which dissociate in the solution.

This model has been used herein to determine the basic parameters of the network such as $\overline{M}_C$ and χ.

2- Experimental

2-1- Materials

Acrylamide (AAm) and N,N'-methylene bisacrylamide (Bis) were purchased from Merck and were used as the base monomer and the cross-linking agent, respectively. Ammonium persulphate (APS) and sodium metabisulfite (SBS) were purchased from Fisher Company and used as the initiator and accelerator, respectively. Sodium chloride, calcium chloride, and sodium sulphate were obtained from Fisher Company as well. A 50 wt% solution in water of ((methacrylamido) propyl) trimethyl ammonium chloride (MAPTAC) was purchased from Aldrich. All reagents were used as received. Double distilled deionised water was used for the synthesis of hydrogels and swelling experiments.

2-2- Experimental Design

Selection of Orthogonal Array (OA) and Assignment of Factors

Standard tables known as OA are used to design the experiment in Taguchi method. An OA with five factors and four levels for each factor was assigned by using Minitab software version 6.3 (Table 1). This OA is particularly designed with the symbol L_{16}. The reaction variables including total monomer concentration (%T), the molar percent of cross-linking agent (%C), the molar percent of dissociable monomer (%MAPTAC), molar ratio of initiator to total monomer (%I) and synthesis temperature are generally important factors in the synthesis of cationic superabsorbent hydrogel. These variables are defined as follows:

$$\%\mathrm{T} = \frac{\text{mass of all monomers (g)}}{\text{volume of water (mL)}}\times 100 \qquad (7)$$

$$\%\mathrm{C} = \frac{\text{mole of (MBAA) in feed solution}}{\text{total mole of monomers in feed solution}}\times 100 \qquad (8)$$

$$\%\,\mathrm{MAPTAC} = \frac{\text{mole MAPTAC in feed}}{\text{total mole of monomers in feed}}\times 100 \qquad (9)$$

$$\%I = \frac{\text{mole of Initiator in feed solution}}{\text{total mole of monomers in feed solution}} \times 100 \tag{10}$$

No homogenous network is formed when T is less than 10%. Previous studies show that increasing T up to more than 40% does not considerably affect the amount of swelling. That is why the values of 10 and 40 are chosen as the lower and the higher limits of this variable [14].

Table 1: Experimental control factors and their levels

No.	Factors	Level 1	Level 2	Level 3	Level 4
1	T (%)	10	20	30	40
2	C (%)	0.05	0.1	0.15	0.2
3	MAPTAC(%)	5	10	15	20
4	Temperature [°C]	30	50	70	90
5	$I \times 10^2$ (%)	4	6	8	10

Four levels for each factor were chosen as shown in Table 2. Therefore, the evaluation of results has been standardized by this method. The results were analyzed statistically by the analysis of variance (ANOVA) method by using aforementioned software.

2- 3- Hydrogel preparation

Cationic hydrogels were synthesized by aqueous free radical copolymerization of acrylamide, MAPTAC and Bis. The monomeric solution was stirred by a mechanical stirrer until a homogeneous solution was obtained. A Teflon coated reactor was kept at 70 ?C in nitrogen atmosphere. Polymerization reaction started by the reaction between SBS and APS after adding certain amount of solutions to the pre-mixed solution, respectively. Polymerization was conducted for 24 hours in order to complete the polymerization reaction. Then the synthesized hydrogel was taken out of the reactor and immersed in distilled water for about 3 days. Afterwards, the samples were dried at the room temperature and ground into small particles (0.05 to 0.2 mm in size).

2-4- Swelling Measurements

Dried hydrogels were poured into a vessel of fine mesh and weighed. The mesh bag was placed in distilled water for 10 days to reach absolute equilibrium. The bath temperature was kept at approximately 24±1°C. Then the mesh was taken out of water, the water on the mesh was dried precisely, the mesh was weighed, and the swelling ratio was calculated by Equation 11. In the swelling experiments in electrolyte solution, the solution was changed every day in order to maintain the salt concentration at a constant level. In addition, while the hydrogel was swelling, the lid of the container was kept closed to prevent evaporation. This process went on for a fortnight to assure retaining of the equilibrium condition. The swelling ratio was calculated by the following equation.

$$q = \frac{mass\ of\ swollen\ gel\ (g)}{mass\ of\ dry\ gel\ (g)} \tag{11}$$

3- Results and Discussion

3-1- Hydrogel Swelling in Distilled Water

The results of the equilibrium swelling of 16 synthesized hydrogels, have been included in Table 3. Swelling experiments were repeated 3 times for every synthesized hydrogel in order to make sure of the accuracy of measurements. The final amount of swelling was the average of the 3 obtained results. The most important feature of superabsorbent hydrogels is their amazing ability to absorb water. As is seen, synthesized hydrogels can absorb a great amount of water.

Table 2: Experimental layout of L_{16} orthogonal array

Exp. No.	T (%)	C (%)	MAPTAC (%)	Polymerization Temp. [°C]	% I × 10^2 (%)
1	10	0.1	5	30	4
2	10	0.2	10	50	6
3	10	0.3	15	70	8
4	10	0.5	20	90	10
5	20	0.1	10	70	10
6	20	0.2	5	90	8
7	20	0.3	20	30	6
8	20	0.5	15	50	4
9	30	0.1	15	90	6
10	30	0.2	20	70	4
11	30	0.3	5	50	10
12	30	0.5	10	30	8
13	40	0.1	20	50	8
14	40	0.2	15	30	10
15	40	0.3	10	90	4
16	40	0.5	5	70	6

Table 3: Experimental results for equilibrium swelling capacity

Trial No. Exp. No.	I	II	III	Avg.
1	142	158	151	150.3
2	358	341	362	353.7
3	464	452	421	445.7
4	273	267	264	268.0
5	265	253	258	258.7
6	52	48	59	53.0
7	455	432	465	450.7
8	92	88	97	92.3
9	132	122	129	127.7
10	105	112	98	105.0
11	65	71	75	70.3
12	41	38	50	43.0
13	158	149	143	150.0
14	53	47	58	52.7
15	52	49	55	52.0
16	21	29	26	25.3

Table 4: The results of ANOVA for various factors

Factor	Degree of freedom	Sums of Squares	Variance	F-Ratio	Contribution of factor (%)
T (%)	3	443274	147758	1779	48.0
C (%)	3	143377	47792	575	15.5
MAPTAC (%)	3	175125	58375	703	19.0
Temperature [°C]	3	42322	14107	170	4.5
I (%)	3	117329	30109	471	13.0

The effect of each parameter on the final swelling ratio was calculated by ANOVA analysis and the results are shown in Figures 1A-E. As is seen in Figure 1-A, hydrogel swelling decreases by increasing the initial concentration of the monomers. As was explained before, it is due to the reduction in the chaining reactions because of increasing monomers concentration. In this way, a network is obtained which is more resistant to deformation (swelling) and therefore, the final amount of the swelling will decrease. Similar results have been obtained in other people's experiments [12, 17].

Figure 1-B shows that as the cross-linking agent increases, the final amount of swelling decreases due to the increase in the cross-links density in the network. As the molar ratio of the cross-linking agents increases, the curve assumes an approximately plateau form. As the amount of the cross-linking agents increases, the length of the chains (the number of monomer units between two successive cross-links) decreases.

When the polyelectrolyte hydrogel swells, the chains reach their maximum length and do not allow the network to swell more. At this point, the free elastic energy of the network becomes infinity. This force is exerted on a direction opposite to that of the network's swelling.

The force is equal to the opposite forces such as mixing and ionic forces, and prevents the network from swelling more. As is expected, the increase in the amount of dissociating monomer (MAPTAC) in the network increases the final amount of swelling through increasing electrostatic forces and the osmotic effects of opposite charges [7, 9 and 23]. This trend is shown in Figure 1-C. When the amount of MAPTAC monomers increases in the network of gel, due to the presence of counter ions, the amount of osmotic pressure difference between bath and gel increases and thus the gel swell more to compensate this difference.

Figures 1-D and 1-E show the effect of the amount of reaction initiator and the temperature on the amount of water absorption by synthesized hydrogels.

Figure (2) shows the changes in the final amount of swelling versus the concentration of the dissociable monomer in a logarithmic scale.

The changes, as are seen, are linear. The slope is about 0.81, indicating that the amount of the swelling changes is proportional to the power 0.81. Gundogan et al. [25] showed that the change in the amount of the swelling is to the power 0.75.

Figure (3) shows the changes in the final amount of swelling versus the concentration of the initial monomer in a logarithmic scale. This trend was also observed by Vasheghani-Farahani et al. [24].

Using Minitab software, the optimized circumstances and the contribution of each factor was performed while the interaction between factors was ignored.

It is seen from the ANOVA results (Table 4) that the most effective factor is the total monomer concentration. Second to that, the amount of dissociable monomer, cross-linking agent, initiator, and temperature are the most effective parameters on the amount of swelling.

After conducting the synthesis of the optimized hydrogel, the equilibrium swelling of this hydrogel was measured in deionised water for three times and the following data was obtained: 3650, 3480, 3590 (g water/ g dried gel). Observed errors can be attributed to the method of equilibrium swelling measurement and the very high equilibrium swelling capacity of the optimized cationic superabsorbent hydrogel. Table 5 classifies the optimized values of each variable in addition to their contribution in the hydrogel swelling in order to obtain the maximum amount of swelling. This optimized hydrogel was used as the sample hydrogel for the swelling experiments done in an electrolytic environment.

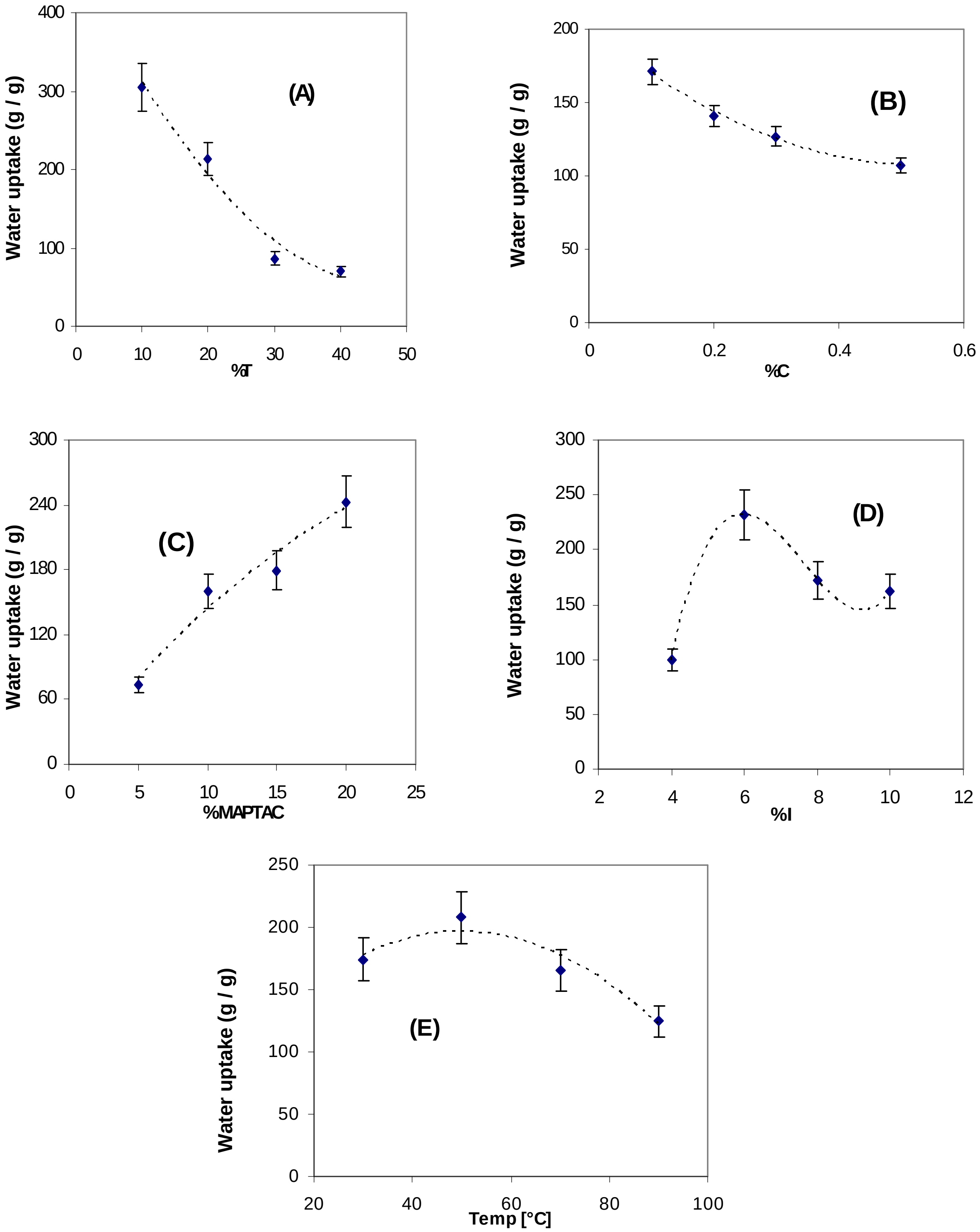

Figure 1: Main effects of each parameter on the equilibrium swelling capacity of superabsorbent hydrogels (A): effect of initial concentration of total monomers, (B): effect of cross-linking agent, (C): effect of amount of MAPTAC, (D): effect of amount of the initiator of the reaction, and (E): effect of polymerisation temperature

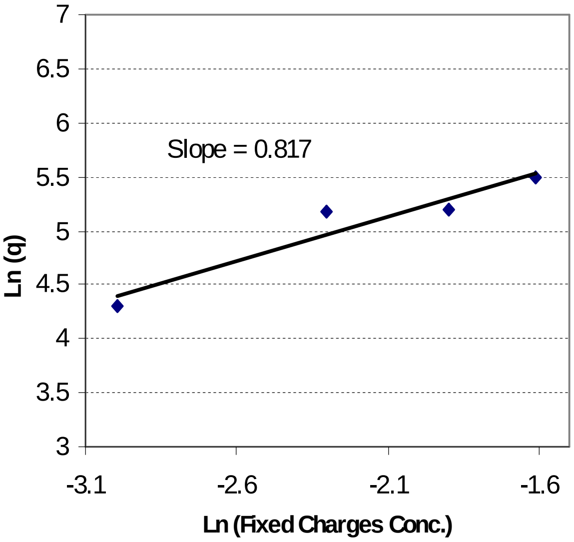

Figure 2: Effect of fixed charges concentration on the equilibrium swelling of gels in distilled water in the logarithmic scale.

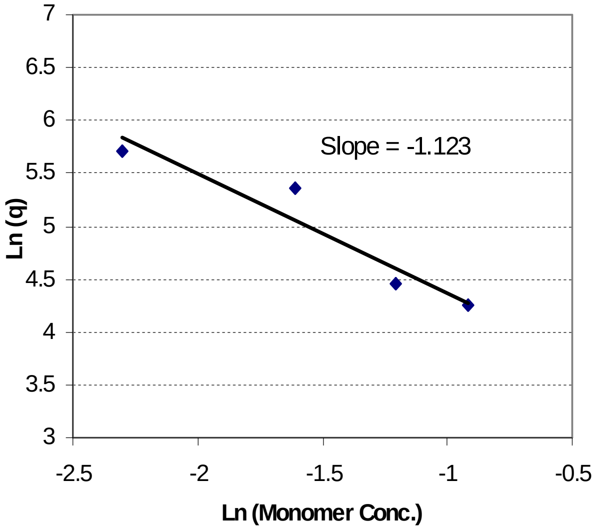

Figure 3: Effect of initial concentration of monomers on the final amount of swelling in the logarithmic scale.

Table 5: Optimum condition and performance, obtained from ANOVA

Factor	Optimum condition (Level Description)	Optimum condition (Level)	Contribution
T (%)	10	1	304.416
C (%)	0.1	1	254.666
MAPTAC (%)	20	4	243.416
Temperature [°C]	50	2	208.666
I (%)	6	2	239.333

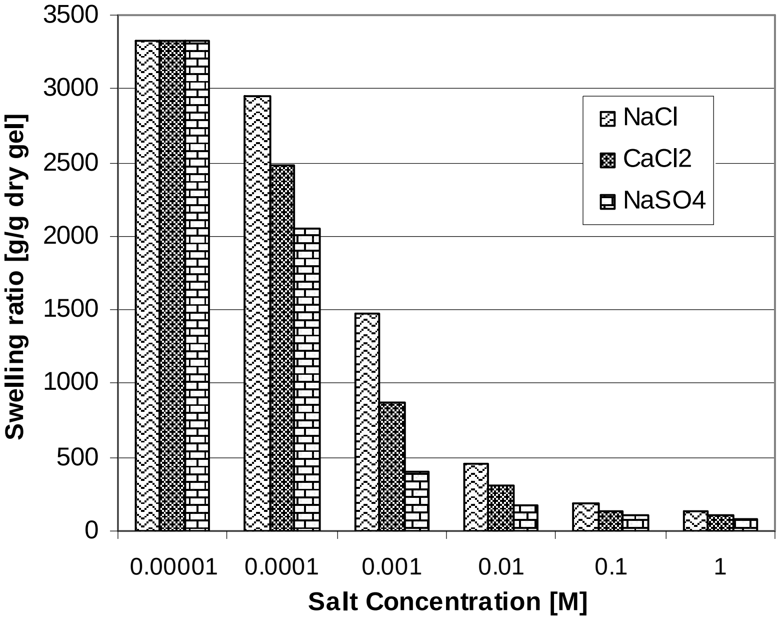

Figure 4: Equilibrium swelling ratio of optimized superabsorbent in 3 different salt solutions with concentrations ranging form 10^{-5} to 1 M.

3-2- Swelling in Electrolytic Solution

Figure (4) shows the equilibrium swelling ratio of the sample hydrogel in different electrolytic solutions with various concentrations. It can be observed that the more the concentration of the solution (ionic strength) is, the less the equilibrium swelling ratio of the hydrogel will be. This can be explained by the effect of counter-ions effect. In low ionic strength, the constant positive charges on the network are approximately equal to the concentration of the surrounding salt solution. Therefore, there will be a high concentration difference between the counter-ions (negative ions) inside and outside the hydrogel. This high amount of concentration difference, results in a high osmotic pressure difference between the hydrogel and the surrounding solution, and consequently, the hydrogel swells more.

As Figure (4) shows, the equilibrium swelling of Na_2SO_4 salt is less than those of the other salts (NaCl and $CaCl_2$) in similar concentrations. The reason is that all the salts solutions completely dissociate in water. The ionic strength of the salts is calculated by the following equation.

$$I = \frac{1}{2}\sum_i C_i z_i^2 \qquad (12)$$

In similar concentrations of the said salt solutions, the ionic strength from top to bottom will be those of Na_2SO_4, $CaCl_2$, NaCl. As the ionic strength increases, less osmotic pressure will be exerted by counter-ions, resulting in a decrease in the swelling [5, 21 and 26].

In higher concentrations (around 1 M) of the said salt solutions, the amount of swelling is approximately independent of the ionic strength. This can be explained by: a) the equal concentration of the ions inside and outside the hydrogel, and the reduction in ionic osmotic pressure; and b) The concentration increase of the ions inside the hydrogel network, as the ionic strength increases. These ions form a shield against the repulsive intra-chain electrostatic forces. Thus, the final amount of swelling decreases. However, in the lower concentrations, the repulsive electrostatic forces are exerted in a more extensive area and the network expands in order to minimize the repulsive free energy [16]. Figure (5) shows this process, schematically.

3-3- Determination of the Network Parameters

If the swelling ratio is assumed to be the ratio of the mass of the swollen hydrogel to that of the dry hydrogel (Equation 11), the volume fraction of the polymer inside the network is calculated by the following equation.

$$\varphi_2 = \left(1 + \frac{\rho_2}{\rho_1} q - \frac{\rho_2}{\rho_1}\right)^{-1} \tag{13}$$

Where ρ_1 is the density of solvent. The above equation will turn into Equation 14 after rearrangement and taking into account the values of mixing, elastic, and ionic portions.

$$-\left(Ln(1-\varphi_2)\Big/\varphi_2^2 + \varphi_2^{-1}\right) + \frac{V_1}{\varphi_2^2}\sum\left(C_i^{gel} - C_i^{solution}\right) = \frac{1}{2}\frac{V_1\rho_2}{\overline{M}_C^{eff}}\left(\varphi_2^{-5/3}\right) + \chi \tag{14}$$

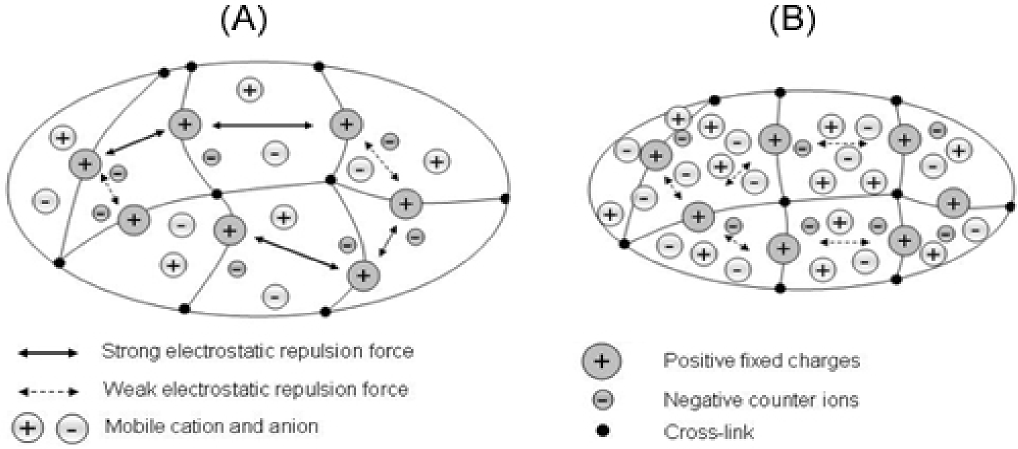

Figure 5: The state of intra-chain electrostatic repulsion force caused by bound positive charges inside the network, (A) low concentration of solution, (B) high concentration of solution.

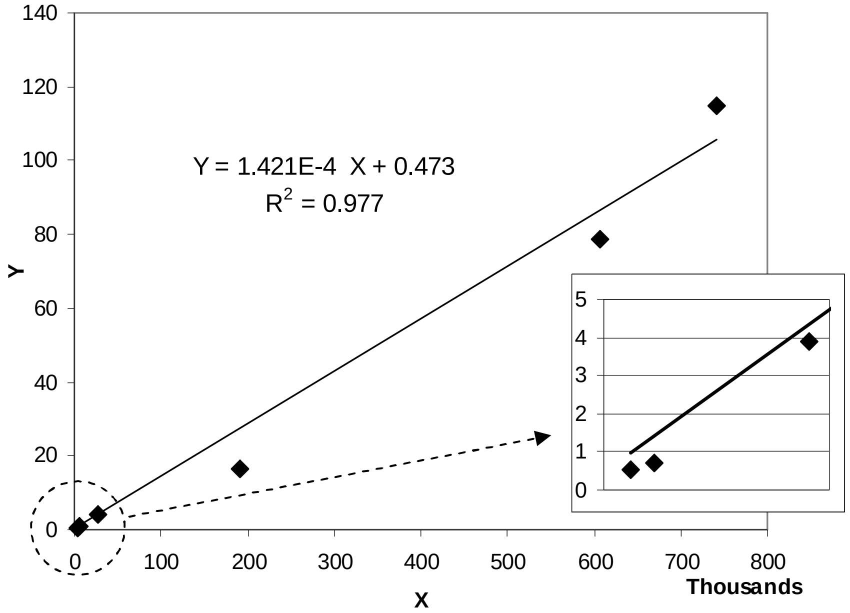

Figure 6: The analysis of experimental data using equation 14. The slope is proportional to cross-links density and intersect demonstrates χ.

A line will be obtained by plotting the left hand side of Equation 14 (Y) versus its first term of the right hand side (X). The slope of this line is proportional to the density of the cross-linking agents and its intercept is equal to the value of χ. Figure (6) shows the drawn line for swelling experiments of the sample polyelectrolyte hydrogel in NaCl salt solution. The straight line shown in this figure is obtained by linear regression of the experimental data. The intercept of this line is 0.473 and $\overline{M}_C$ is equal to 85500 g/mol. The Flory interaction coefficient for acrylamide based hydrogels is equal to 0.48. The meagre difference (0.007) can be caused by the change in the hydrophilic / hydrophobic characteristics of the network due to the presence of MAPTAC monomers.

The value for $\overline{M}_C$ calculated by stoichiometry is 35500 g/mol. This value is very different from the model value. It indicates that approximately 60% of the cross-linking agents are wasted in ineffective cross-links.

4- Conclusion

Cationic polyelectrolyte acrylamide based hydrogels were synthesized through a free radical polymerization reaction. The effects of various parameters such as the initial concentration of total monomers, the amount of the cross-linking agent, the amount of dissociable monomers, the amount of the reaction initiator, and the temperature of the polymerization reaction on the swelling of the synthesized hydrogels in distilled water were studied. The synthesis conditions of superabsorbent hydrogels were optimized by Taguchi method and the maximum water absorbency (3570 g/g) was achieved. The results showed that the initial concentration of monomers has the most and the reaction temperature has the least effect on swelling. Increasing the initial concentration of the monomers and the cross-linking agents in the feedstock solution results in the reduction of swelling. Due to the creation of proper osmotic pressure, employment of dissociable monomer in the gel structure results in an increase in the gel swelling. The Taguchi method was found to be promising tool to obtain the optimum conditions for such study. Swelling experiments carried out in various electrolytic solutions with different ionic strength shows that a phase transformation occurs continuously by changing the ionic strength of the surrounding solution. Increasing the ionic strength for a specific salt decreases the swelling. In addition, in higher concentrations of the salt solutions (around 1 M), the swelling behavior of the hydrogels will be somehow independent of both the solution and its concentration due to an increase in the ionic strength of the solution. By using the presented model, the experimental data were analyzed and the cross-linking efficiency for the polymerisation reaction was calculated to be about 40%.

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