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Dynamic swelling behavior of γ-radiation induced polyelectrolyte poly(AAm-*co*-CA) hydrogels in urea solutions

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Abstract

The aim of this study was to investigate the equilibrium swelling properties in urea solutions of γ-radiation induced polyelectrolyte copolymeric hydrogels consisting of acrylamide (AAm) and crotonic acid (CA). Poly(acrylamide-*co*-crotonic acid), poly(AAm-*co*-CA) hydrogels containing different amounts of CA were obtained in the form of rods after radiation. Swelling experiments were performed in aqueous urea solutions at 25 °C, gravimetrically. The hydrogels showed large extents of swelling in aqueous (urea/water) media the swelling being highly dependent on the chemical composition of the hydrogels and irradiation dose. The percentage swelling of poly(AAm-*co*-CA) hydrogels was between 1160 and 4250%, while that of the AAm hydrogels was between 670 and 900%. The diffusional exponent values (*n*) are between 0.51 and 0.66, hence the diffusion of urea/water into the hydrogels is *non-Fickian*. Equilibrium urea/water contents of the hydrogel systems were changed between 0.870 and 0.977.

Keywords: γ-Radiation; Swelling; Diffusion; Acrylamide/crotonic acid; Hydrogel; Urea

1. Introduction

Hydrogels are polymers in a three-dimensional network arrangement, able to retain large amounts of water. In order to keep the spatial structure, the polymer chains are usually physically or chemically crosslinked. The importance of hydrogels in the biomaterial field is justified by some unique characteristics: the elastomeric and soft nature of the hydrogels minimizes mechanical and frictional irritation to the tissues and the very low interfacial tension contributes to reducing protein adsorption and cell adhesion. Due to their swelling capacity, hydrogels can be easily rinsed to remove reagent residues. On the other hand, the large water content makes hydrogels a special class of materials. Their network structure is the result not only of

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covalent bonding but also ionic, hydrogen or even van der Waals interactions. The unique physical properties of hydrogels such as high water affinity, high thermal and mechanical stability, biocompatibility, allies a variety of industrial and biomedical applications (Peppas and Mikos, 1986; Kim et al., 1992; Evmenenko et al., 1999; Rosiak and Yoshii, 1999; Byrne et al., 2002; Gupta et al., 2002; Hennink and van Nostrum, 2002; Lopes and Felisberti, 2003; Paxton et al., 2003; Rosso et al., 2003; Magnin et al., 2004; Peppas, 2004).

Water sorption by hydrogels accounts for a great number of biomedical and technological applications such as artificial implants, contact lens, enzyme immobilization, catheters, wound dressings, biosensors, etc. (Peppas and Mikos, 1986; Kim et al., 1992; Rosiak and Yoshii, 1999; Gupta et al., 2002; Hennink and van Nostrum, 2002; Shantha and Harding, 2003).

Adsorption of species such as enzymes and amino acids, desalination of sea water, ultrafiltration and purification of aqueous solutions containing colloids, micro- and macroparticles, or other biochemical/physiological species in aqueous media have been studied for use industrial and/or biotechnological processes (Gombotz and Hoffmann, 1986; Güven et al., 1999; Chen and Chiu, 2000; Saraydın et al., 2002; Magnin et al., 2004; Saraydin et al., 2004; Karadag et al., 2005). Hydrogels can be used as composite membranes for various enzymes, for example, for immobilization of urease enzyme, various composite hydrogel membranes can be used (Chen and Chiu, 2000; Karadag et al., 2005). Urease is a highly specific enzyme. It catalyzes the hydrolysis of urea to ammonium and carbon dioxide. It has been immobilized for analytical and biomedical purposes. One of the major applications of immobilized urease is the direct removal from blood for detoxification, or in the dialysis regeneration systems of artificial kidney machines. Other applications of immobilized urease will be in a bioreactor for the conversation of urea present in fertilizer wastewater effluents to ammonia and carbon dioxide or in the food industry for the removal of urea from beverages and foods (Chen and Chiu, 2000).

Urea is one of the main toxic wastes in the dialysate solution from hemodialysis. The most effective way of removing urea from aqueous solutions is the utilization of immobilized urease as no efficient adsorbent is available for urea. On the other hand, urea has a great importance in biological systems (Karadag et al., 2005).

Research on the use of radiation in the production of hydrogels has become intense during more than a decade; interest has grown continuously, and a large number of papers have been published last years (Rosiak and Ulanski, 1999; Jabbari and Nozari, 2000; Clough, 2001; Luago and Malmonge, 2001;) Numerous applications have been found or envisioned for these materials, particularly in the biomedical area. Some special using area of hydrogels are wound dressing, soft contact lenses, controlled-released drug delivery systems, biocompatibility, artificial skin, water absorbents, and adsorbents for metal ions or enzymes for purification or catalysis applications (Kaetsu, 1995; Safrany, 1997; Rosiak and Yoshii, 1999; Bhattacharya, 2000; Saraydın et al., 2002; Karadag et al., 2004).

It was of interest to swelling properties of poly(AAm-*co*-CA) hydrogels in urea solutions for new hydrogels synthesis for urea treatment as new membranes or crosslinked polymeric carriers, or adsorption. The present paper reports a swelling study in urea solutions of a novel type of hydrogel prepared acrylamide and crotonic acid by γ-radiation technique.

2. Materials and methods

2.1. Experimental materials and preparation

The sources of water, the monomers: acrylamide (AAm) and crotonic acid (CA), γ-irradiation doses were given before (Saraydin et al., 1995). The method of preparation of the gamma-radiation induced poly(AAm-*co*-CA) hydrogel systems was the same as described in our earlier communication (Saraydın et al., 1995).

For preparation of crosslinked poly(AAm-*co*-CA) copolymers, acrylamide (AAm) weighing 1 g was dissolved in 1 mL aqueous solutions of 0, 20, 40 and 60 mg crotonic acid (CA). These solutions were placed in PVC straws of 4 mm diameter and irradiated at 2.00, 2.60, 3.73, 4.65, 5.20 and 5.71 kGy in air at ambient temperature in a ^{60}Co Gammacell 220 type γ-irradiator at a fixed dose rate of 0.91 kGy h^{-1}. The dose rate was determined by the conventional Fricke dosimeter. Fresh hydrogels obtained in long cylindrical shapes were cut into pieces of 3–4 mm length. They were dried in air

and vacuum and stored for swelling (Saraydin et al., 1995).

Urea was provided from MERCK (Darmstadt, Germany).

2.2. Swelling measurements in urea solutions

A fundamental relationship exists between the swelling of a polymer in a solvent and the nature of the polymer and the solvent. Aqueous urea solutions have been prepared as 0.01 and 0.03 M.

Dried hydrogels were left to swell in distilled water at 25 ± 0.1 °C to determine the parameters of swelling and diffusion. Swollen gels that were removed from the water bath at regular intervals were dried superficially with filter paper, weighed, and placed in the same bath.

The swelling percent, $S\%$ of the hydrogels in the aqueous urea solutions was calculated from the following relation:

$$S\% = \frac{w_t - w_0}{w_0} \times 100 \quad (1)$$

where w_t is the mass of the swollen gel at time t and w_0 is the mass of the dry gel at time 0.

3. Results and discussion

3.1. Equilibrium swelling studies

The urea/water intake of initially dry hydrogels was followed for a period of time, gravimetrically. Swelling isotherms of the hydrogels were constructed and representative swelling curves are shown in Fig. 1.

Fig. 1 shows that swelling increases with time up to certain level, then levels off. This value of swelling may be called as the equilibrium swelling percent ($S_{eq}\%$). $S_{eq}\%$ of poly(AAm-*co*-CA) hydrogels is used for the calculation of swelling characterization parameters. $S_{eq}\%$ of poly(AAm-*co*-CA) hydrogels are given Table 1.

Table 1 shows that $S_{eq}\%$ of AAm hydrogels are 670–901%, but $S_{eq}\%$ of poly(AAm-*co*-CA) hydrogels are 1158–4246% with the incorporation of CA groups into AAm hydrogels. The chemical structure, or possible binding mechanism of poly(AAm-*co*-CA) hydrogel systems was demonstrated simply on Fig. 2. As it can be seen from Fig. 2, hydrophilicity of poly(AAm-*co*-CA) copolymers becomes greater than that of AAm, so the swelling of poly(AAm-*co*-CA) copolymers is greater than the swelling of AAm hydrogels.

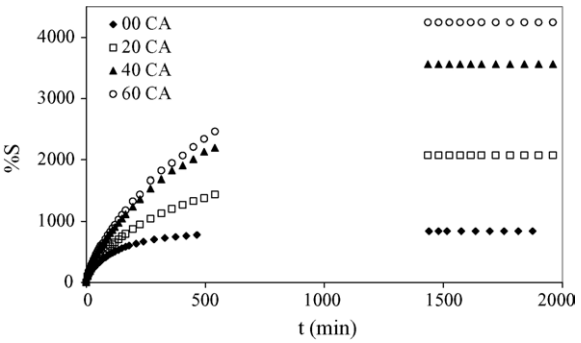
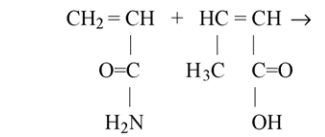


Fig. 1. Swelling isotherms of poly(AAm-*co*-CA) hydrogels in 0.01 M urea solutions. Total dose given 2.60 kGy.

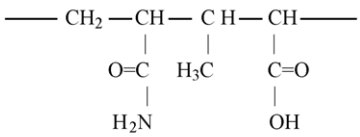
Table 1
Equilibrium swelling percent of poly(AAm-*co*-CA) hydrogel systems in 0.01 M urea solutions

Dose (kGy)	Equilibrium swelling percent, $S_{eq}\%$			
	00 mg[a]	20 mg[a]	40 mg[a]	60 mg[a]
2.00	901	1963	3884	3977
2.60	839	2073	3562	4246
3.73	872	1555	3064	3614
4.65	768	1330	1677	2695
5.20	826	1158	1400	2330
5.71	670	1194	1938	2791

[a] CA.



Acrylamide (AAm) + Crotonic acid (CA)



Poly(acrylamide/crotonic acid), poly(AAm-*co*-CA) copolymer

Fig. 2. Chemical structures of monomers and possible binding mechanism between acrylamide and crotonic acid for crosslinked poly(AAm-*co*-CA) copolymers.

In Table 1, S_{eq}% of the hydrogels decreased with the increase in the irradiation dose and, increased with the CA content in the copolymers. S_{eq}% of poly(AAm-*co*-CA) hydrogels is higher than S_{eq}% of AAm hydrogels. The reason of this is the hydrophilic groups on the CA. As it can be seen from Fig. 2, the more hydrophilic groups in the poly(AAm-*co*-CA) get the more the swelling of the poly(AAm-*co*-CA) hydrogels.

The increase in amount of absorbed dose lessens the number of small chains. Thus, hydrogels exposed higher doses has higher crosslink density than hydrogel exposed lower doses. This means that high amount adsorbed dose decrease the number average molar mass between crosslinks while low amount of adsorbed dose increase the number average molar mass between crosslinks (Saraydin et al., 1995).

On the other hand, the values of the equilibrium swelling percent of swollen in urea solutions poly(AAm-*co*-CA) hydrogels are bigger than the hydrogels swollen in water. The values of the hydrogels swollen in water were between 650 and 2300% (Saraydin et al., 1995). The reason of this different behavior is the hydrophilic character of urea molecules. Urea molecule has got more hydrophilic sites, as NH_2 and C=O. When, urea molecules have interacted with much water, so, there has been much swelling than swelling values in water, also. That is way, urea molecules have got hydrophilic groups, more swelling values have been observed when the hydrogels swollen in aqueous urea solutions. On the other hand, the urea solutions will act as a weak base, which interacts stronger with the carboxylic acid of CA. Here main characteristic effects are the hydrophilic character of urea molecules and behavior of urea molecules as a weak base groups. So, the more hydrophilic groups in the aqueous urea solutions get the more the swelling of the poly(AAm-*co*-CA) hydrogels. In the presence of urea, swelling of poly(AAm-*co*-CA) hydrogels can easily follow the change of the hydrogen-bonded structure of water and polymer–solvent interaction.

4. Swelling kinetics

In order to examine the controlling mechanism of the swelling processes, several kinetic models are used to test experimental data. The large number and array of different chemical groups on the poly(AAm-*co*-CA) chains (e.g., amide, carboxyl) imply that there are many types of polymer–solvent interactions. It is probable that any kinetics is likely to be global. From a system design viewpoint, a lumped analysis of swelling rates is thus sufficient to the practical operation.

A simple kinetic analysis is a second order equation in the form of

$$\frac{dS}{dt} = k_{2,S}(S_{eq} - S)^2 \quad (2)$$

where $k_{2,S}$ is the rate constant of swelling and S_{eq} (or S_{eq}%) denotes the swelling percent at equilibrium. After definite integration by applying the initial conditions $S = 0$ at $t = 0$ and $S = S$ at $t = t$, Eq. (2) becomes

$$\frac{t}{S} = A + Bt \quad (3)$$

where A is reciprocal of initial swelling rate r_0 or $1/k_{2,S}S_{eq}^2$ and B is inverse of the degree of swelling at equilibrium form (Peniche et al., 1997; Garcia et al., 2004; Saraydin et al., 2004).

To test the kinetics model, t/S versus t graphs are plotted and representative graphs are illustrated in Fig. 3. The calculated kinetic parameters are tabulated in Table 2.

As can be seen from Table 2, kinetics model is agreement with swelling experiments, since, as depicted in Table 2, S_{eq}% (theoretical) or S_{eq}%$_{max}$ is increased with CA content and decreased with irradiation doses. Here, the swelling rate constant is increased with irradiation doses content and decreased with CA. This is plausible since the hydrophilicity of the network is enhanced with the extent of CA groups in structure (Fig. 2). However, the increase in the absorbed

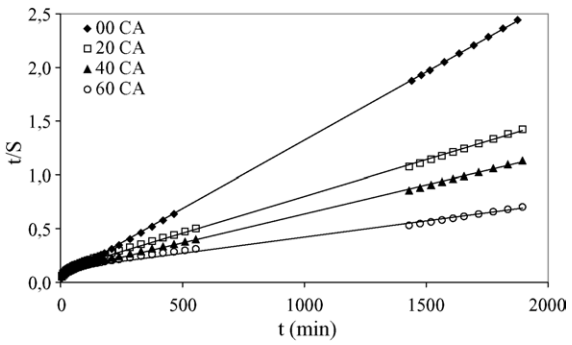


Fig. 3. Swelling kinetics curves of poly(AAm-*co*-CA) hydrogels in 0.01 M urea solutions. Total dose given 4.65 kGy.

Table 2
Swelling kinetics parameters of poly(AAm-*co*-CA) hydrogel systems in 0.01 M urea solutions

Dose (kGy)	The initial swelling rate, r $(dS/dt)_0$; $g_{water}/(g_{gel}$ min)			
	00 mg[a]	20 mg[a]	40 mg[a]	60 mg[a]
2.00	11.71	8.22	10.17	8.73
2.60	10.89	8.62	10.08	9.33
3.73	13.21	9.73	9.00	13.04
4.65	19.31	8.59	10.20	8.29
5.20	12.77	8.70	9.07	9.60
5.71	9.90	9.72	9.90	10.67
	The swelling rate constant, $k_s \times 10^6$; $g_{gel}/(g_{water}$ min)			
2.00	13.00	1.60	0.41	0.30
2.60	14.00	1.50	0.51	0.28
3.73	16.00	3.33	0.62	0.71
4.65	31.17	4.01	2.96	0.75
5.20	17.19	5.52	3.85	1.31
5.71	20.26	5.86	2.08	0.99
	The theoretical equilibrium swelling, $S_{eq}\%_{max}$; g_{water}/g_{gel}			
2.00	943	2269	4963	5364
2.60	877	2393	4456	5757
3.73	909	1709	3798	4283
4.65	787	1463	1856	3316
5.20	862	1256	1534	2705
5.71	699	1287	2184	3279

[a] CA.

dose makes the structure tighter for water to diffuse, in spite of its high hydrophilic content. So it is important to note that extent of irradiation dose determines the swelling rate by increasing hydrophilicity, but reduced the molar mass between crosslinks. So, these two phenomena compete to determining the rate of swelling. Here, again, there is no important different between swelling kinetics parameters in different concentration of aqueous urea solutions, too.

4.1. Swelling rate coefficients

Swelling characteristics, particularly the rate of aqueous swelling or water or/and aqueous solutions uptake was followed some methods.

Fig. 4 shows that equilibrium swelling percent, *S*% for the poly(AAm-*co*-CA) hydrogels versus the square root of immersion time for the first 60% of the fractional uptake (Uruzhizaki et al., 1990; Karadag et al., 2005). Excellent linear correlations were observed. Linear slopes of all poly(AAm-*co*-CA) hydrogel systems swelling behaviors in Fig. 4 were assumed to represent relative swelling rate coefficients ($k_{0.5}$). The swelling rate coefficients are tabulated in Table 3. Swelling rate coefficients of poly(AAm-*co*-CA) hydrogels linearly increased by increasing the CA contents and they decreased with the irradiation dose. Furthermore, it can be said that the hydrogels swells with increase of CA than with increase of irradiation dose.

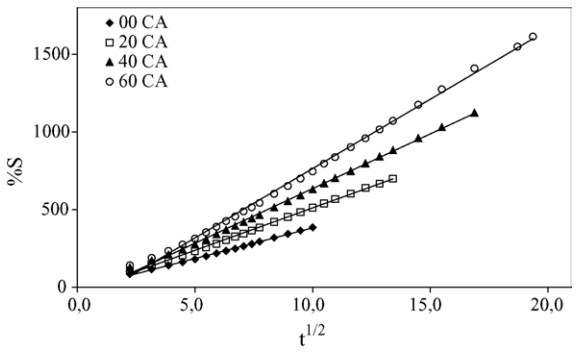


Fig. 4. Plots of swelling rate for poly(AAm-*co*-CA) hydrogels in 0.01 M urea solutions. Total dose given 5.71 kGy.

Table 3
Swelling rate coefficients ($k_{0.5}$) of poly(AAm-*co*-CA) hydrogel systems in 0.01 M urea solutions

Dose (kGy)	$k_{0.5}$			
	00 mg[a]	20 mg[a]	40 mg[a]	60 mg[a]
2.00	54.5	67.1	110.2	107.8
2.60	49.5	67.6	103.5	115.3
3.73	54.7	60.6	88.5	115.2
4.65	58.2	57.0	69.4	81.5
5.20	49.7	51.4	56.7	78.0
5.71	39.4	54.7	70.4	89.3

[a] CA.

As it can be seen in Table 3, there are no important differences between swelling rate coefficients ($k_{0.5}$) of the hydrogel systems.

4.2. Diffusion

When a glassy hydrogel is brought into contact with water, water diffuses into the hydrogel and the network expands resulting in swelling of the hydrogel. Diffusion involves migration of water into pre-existing or dynamically formed spaces between hydrogel chains. Swelling of the hydrogel involves larger segmental motion resulting, ultimately, in increased separation between hydrogel chains.

Analysis of the mechanisms of water diffusion into swellable polymeric systems has received considerable attention in recent years, because of important applications of swellable polymers in biomedical, pharmaceutical, environmental, and agricultural engineering.

The following equation is used to determine the nature of diffusion of penetrant into hydrogels.

$$F = kt^n \quad (4)$$

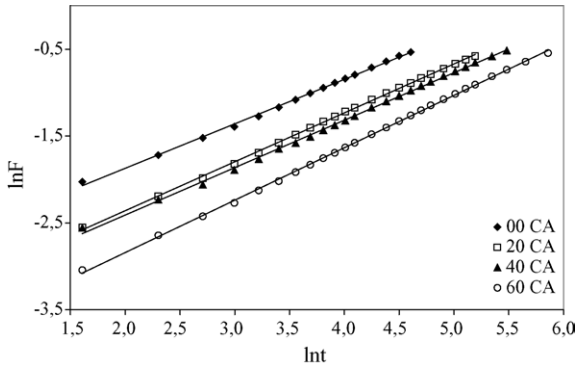


Fig. 5. Plots of $\ln F$ vs. $\ln t$ for poly(AAm-*co*-CA) hydrogels in 0.01 M urea solutions. Total dose given 5.20 kGy.

where F is the fractional uptake at time t, k a constant incorporating characteristic of the macromolecular network system and the penetrate, and n is the diffusional exponent, which is indicative of the transport mechanism (Peppas and Franson, 1983; Saraydin et al., 2004). Eq. (4) is valid for the first 60% of the fractional uptake. Fickian diffusion and Case II transport are defined by n values of 0.5 and 1, respectively. Anomalous transport behavior (non-Fickian diffusion) is intermediate between Fickian and Case II. That is reflected by n between 1/2 and 1 (Peppas and Franson, 1983; Saraydin et al., 2004).

For radiation induced poly(AAm-*co*-CA) hydrogels, $\ln F$ versus $\ln t$ graphs is plotted and representative results are shown in Fig. 5. Diffusion exponents (n) and diffusion constants (k) are calculated from the slopes and intercepts of the lines, respectively, and are listed in Table 4.

Table 4 shows that the number determining the type of diffusion (n) is over 0.50. They are between 0.51 and 0.66. Hence, the diffusion of water into the super absorbent hydrogels is generally found to have a non-

Table 4
Diffusion exponents (n) and diffusion constants (k) of poly(AAm-*co*-CA) hydrogel systems in 0.01 M urea solutions

CA (mg)	Dose (kGy)											
	2.00		2.60		3.73		4.65		5.20		5.71	
	n	k ($\times 10^2$)	n	k ($\times 10^2$)	n	k ($\times 10^2$)	n	k ($\times 10^2$)	n	k ($\times 10^2$)	n	k ($\times 10^2$)
00	0.59	3.6	0.57	3.9	0.56	4.4	0.52	6.8	0.51	5.5	0.51	5.3
20	0.63	1.5	0.59	1.9	0.54	3.0	0.61	2.3	0.56	3.1	0.54	3.5
40	0.66	1.0	0.63	1.2	0.60	1.5	0.60	2.2	0.55	3.0	0.56	2.4
60	0.66	1.0	0.66	1.0	0.62	1.4	0.64	1.2	0.60	1.7	0.59	1.7

Fickian character (Peppas and Franson, 1983; Saraydin et al., 2004). When the diffusion type is anomalous behavior, the relaxation and diffusion time are of the same order of magnitude. As solvent diffuses into the hydrogel, rearrangement of chains does not occur immediately.

Diffusion constants (k) of poly(AAm-*co*-CA) hydrogels are between 1.0×10^{-2} and 6.8×10^{-2}. Diffusion constants increase with the increasing of dose, but there has been seen decreasing with increase content of CA. The reason of these effects is the hydrophilic characteristics of CA.

The study of diffusion phenomena of water in hydrogels is of value in that it clarifies polymer behavior. For hydrogel characterization, the diffusion coefficients can be calculated by various methods. The short time approximation method is used for the calculation of diffusion coefficients of poly(AAm-*co*-CA) hydrogels (Am Ende and Peppas, 1997; Saraydin et al., 2004). The short time approximation is valid for the first 60% of initial swelling.

The diffusion coefficients of the cylindrical poly(AAm-*co*-CA) hydrogels are calculated from the following relations:

$$F = 4\left[\frac{Dt}{\pi r^2}\right]^{1/2} - \pi\left[\frac{Dt}{\pi r^2}\right] - \frac{\pi}{3}\left[\frac{Dt}{\pi r^2}\right]^{3/2} + \cdots \quad (5)$$

where D is in $cm^2\ s^{-1}$, t in s and r is the radius of a cylindrical polymer sample. A comparison of Eqs. (4) and (5) shows the semi-empirical Eq. (4) with $n = 0.5$ and $k = 4(D/\pi r^2)^{1/2}$.

For hydrogels, F versus $t^{1/2}$ plots are constructed and representative results are shown in Fig. 6. The diffusion coefficients were calculated from the slope of the lines. The values of diffusion coefficient determined for the hydrogels are listed in Table 5.

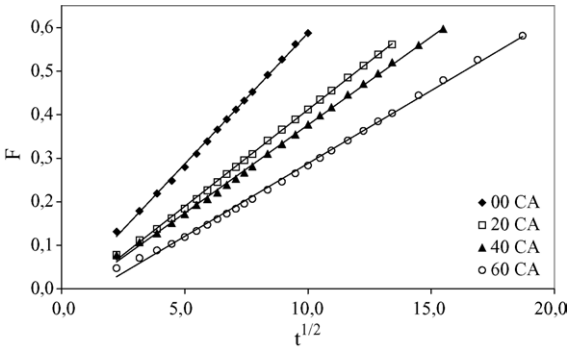


Fig. 6. Plots of F vs. $t^{1/2}$ for poly(AAm-*co*-CA) hydrogels in 0.01 M urea solutions. Total dose given 5.20 kGy.

Table 5 shows that the values of the diffusion coefficient of the poly(AAm-*co*-CA) hydrogels vary from 40.5×10^{-6} to $108.4 \times 10^{-6}\ cm^2\ s^{-1}$ for 0.01 M urea solutions.

4.3. Equilibrium urea/water content

The urea/water absorbed by poly(AAm-*co*-CA) hydrogels is quantitatively represented by the equilibrium urea/water content (EUWC) (Tighe, 1986; Kim et al., 2003; Karadag et al., 2004), where

$$\text{EUWC} = \frac{w_{eq} - w_0}{w_{eq}} \quad (6)$$

Here, w_{eq} is the weight of the swollen gel at time t (equilibrium) and w_0 is the weight of the dry gel at time 0. The values of EUWC of all poly(AAm-*co*-CA) hydrogel systems were calculated. The values of EUWC of the hydrogels are tabulated in Table 6. All EUWC values of the hydrogels (0.8920–0.9770) were greater than the percent water content values of the body about 0.60 (or 60%). Thus, the poly(AAm-*co*-CA) hydrogels exhibited fluid contents similar to those of living tissues.

Table 5
Diffusion coefficients ($cm^2\ s^{-1}$) of poly(AAm-*co*-CA) hydrogel systems in 0.01 M urea solutions

CA (mg)	Dose (kGy)					
	2.00 D ($\times 10^6$)	2.60 D ($\times 10^6$)	3.73 D ($\times 10^6$)	4.65 D ($\times 10^6$)	5.20 D ($\times 10^6$)	5.71 D ($\times 10^6$)
00	56.2	61.5	60.5	108.4	72.9	83.2
20	40.5	46.1	57.8	51.9	58.9	72.7
40	55.1	66.0	55.2	62.2	56.8	59.6
60	51.9	47.2	74.3	56.2	57.3	63.1

Table 6
Equilibrium urea/water content (EUWC) of poly(AAm-*co*-CA) hydrogel systems in 0.01 M urea solutions

Dose (kGy)	Equilibrium urea/water content, EUWC			
	00 mg[a]	20 mg[a]	40 mg[a]	60 mg[a]
2.00	0.9002	0.9515	0.9749	0.9755
2.60	0.8935	0.9540	0.9727	0.9770
3.73	0.8971	0.9396	0.9684	0.9731
4.65	0.8848	0.9301	0.9437	0.9642
5.20	0.8920	0.9205	0.9333	0.9588
5.71	0.8702	0.9227	0.9509	0.9654

[a] CA.

Table 7
Urea/water sorption rate constants (K_{uw}) of polyAAm-*co*-CA) hydrogel systems in 0.01 M urea solutions

Dose (kGy)	K_{uw} ($\times 10^3$)			
	00 mg[a]	20 mg[a]	40 mg[a]	60 mg[a]
2.00	7.2	2.5	1.6	1.6
2.60	7.1	2.3	1.8	1.5
3.73	8.0	3.3	1.8	2.2
4.65	12.1	3.8	3.5	1.9
5.20	7.8	4.2	3.5	2.4
5.71	7.5	4.4	2.8	2.2

[a] CA.

4.4. Urea/water sorption rate

Other important diffusion parameter can be 'urea/water sorption rate constant', K_{uw}. This parameter can be calculated by the urea/water sorption equation (Ali et al., 2003; Karadag et al., 2004, 2005); this equation is below.

$$-\ln\left[1-\left(\frac{m_t}{m_s}\right)\right] = K_{uw}t + E \quad (7)$$

where t is sorption time, K_{uw} the urea/water sorption rate constant, m_t the sorption urea/water amount at time (t), m_s an equilibrium sorption urea/water amount at equilibrium and E is a constant. The plots of $-\ln(1-F)$ versus t, where $F = m_t/m_s$, are shown in Fig. 7. The urea/water sorption rate constants of the poly(AAm-*co*-CA) hydrogels having different CA contents calculated from the slope of the plots, and they are tabulated at Table 7. They are changed among range 1.5×10^{-3} and 12.1×10^{-3} for 0.01 M urea concentration solutions. The results presented in Table 7 showed that urea/water sorption rate constant of acrylamide hydrogels is higher than that of poly(AAm-*co*-CA) hydrogels. It is seen that urea/water diffusion is more stable into AAm hydrogel systems. If CA contents are increased in poly(AAm-*co*-CA) hydrogels, the sorption rate of urea/water amount is decreased. The reason of this may be the hydrophilic characteristics of CA. CA molecules may interact with water molecules, and sorption may be more slowly. These results are parallel to the swelling kinetics parameters presented in Table 2, too.

4.5. Effect of urea concentration

For investigation the effect of urea concentration onto swelling properties of poly(AAm-co-CA) hydrogels, 0.03 M concentration of urea solution was prepared (Fig. 8). Only 4.65 kGy irradiated poly(AAm-co-CA) hydrogels were used at dynamic swelling studies. At the end of swelling studies, calculated some swelling and diffusional parameters are listed at Table 8. As it can be seen from Table 8, there are

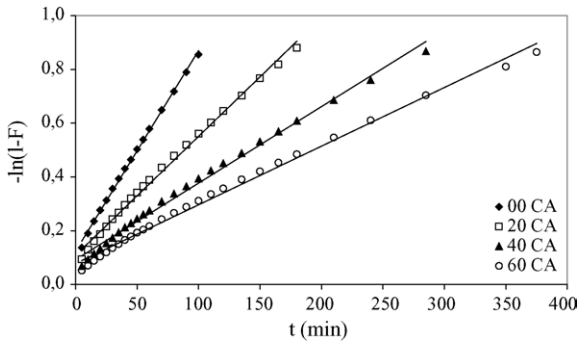


Fig. 7. Plots of $-\ln(1-F)$ vs. t for poly(AAm-*co*-CA) hydrogels in 0.01 M urea solutions. Total dose given 5.71 kGy.

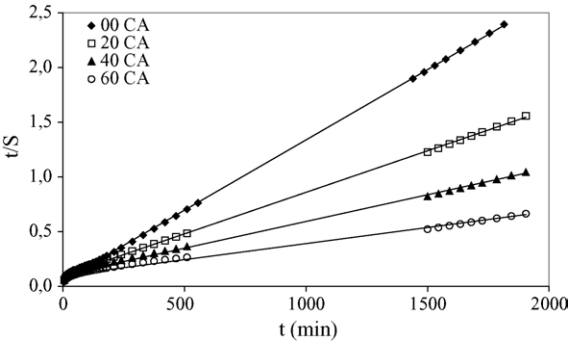


Fig. 8. Swelling kinetics curves of poly(AAm-*co*-CA) hydrogels in 0.03 M urea solutions. Total dose given 4.65 kGy.

Table 8
Some swelling, diffusion and swelling kinetic parameters of poly(AAm-*co*-CA) hydrogel systems in 0.03 M urea solutions

CA (mg)	00	20	40	60
S_{eq}%	758	1223	1825	2872
n	0.54	0.62	0.64	0.64
k ($\times 10^2$)	6.2	2.5	1.7	1.3
D ($\times 10^6$)	114.9	60.4	72.1	72.4
EWUC	0.8835	0.9244	0.9481	0.9663
r $(dS/dt)_o$	18.15	9.94	9.52	10.26
k_s ($\times 10^6$)	29.75	5.72	2.27	0.88
S_{eq}%$_{max}$	781	1318	2049	3406
$k_{0.5}$	57.3	59.6	71.3	91.8
K_{uw} ($\times 10^3$)	11.8	4.7	3.2	2.1

Total dose given 4.65 kGy.

no important differences between all parameters. For example equilibrium swelling percent of poly(AAm-co-CA) hydrogels γ-ray induced 4.64 kGy, are ranged 768–2695% in 0.01 M urea solutions, and the values of equilibrium swelling percent of the same hydrogel system has been calculated as 758–2872% in 0.03 M urea solutions. The same characteristic results were found approximately, all other swelling and diffusional parameters.

5. Conclusion

Poly(AAm-*co*-CA) hydrogels showed high urea/water absorbency. The equilibrium swelling percent of the hydrogel systems were changed between 670 and 4250%. The reason for high swelling percent of the poly(AAm-*co*-CA) hydrogels is the hydrophilic character of urea molecules and the capability of hydrogen bonding for urea molecules with water. It was seen that swelling of poly(AAm-*co*-CA) hydrogels in aqueous urea solutions increased with the increasing of content of CA. The values of equilibrium urea/water contents of the hydrogel systems were changed between 0.870 and 0.977. This data may be important about for poly(AAm-*co*-CA) hydrogel systems as a biomaterial. It can be concluded from the data presented in this paper, that is the poly(AAm-*co*-CA) hydrogels are appropriate matrix for pharmaceutical formulations and for biotechnological applications due its, favourable physicochemical properties. The poly(AAm-*co*-CA) hydrogels reported can be used to carry substances in an aquatic, urea/water field for pharmaceutical important differences of swelling results at different urea concentrations, agricultural, environmental and biomedical applications. The utilization of these types of hydrogels, in biomedicine, controlled drug delivery, pharmaceuticals, agriculture, biotechnology, environment, sorption, separation, purification, immobilization and enrichment of some species makes hydrogel more popular.

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