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Swelling Studies of Copolymeric Acrylamide/Crotonic Acid Hydrogels as Carriers for Agricultural Uses

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ABSTRACT

In this study, highly swollen acrylamide/crotonic acid hydrogels (in a rod form) containing some inorganic salts such as ammonium nitrate, potassium nitrate and ammonium sulphate used as fertilizer, an agricultural drug such as Dalapon (sodium 2,2-dichloropropionate) and two crosslinkers such as ethylene glycol dimethacrylate and 1,4-butandiol dimethacrylate were prepared by copolymerization of acrylamide and crotonic acid with γ-radiation. As a result of swelling tests, the influence of γ-ray dose and relative content of crotonic acid on the swelling properties, the diffusional behavior of water, diffusion coefficients and network properties of the hydrogel systems were examined. Acrylamide/crotonic acid hydrogels containing these salts and agricultural drug were swollen in the range 2045–400% in water, while polyacrylamide hydrogels swelled in the range 660–700%. Water intake of hydrogels followed a nonFickian-type diffusion. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: swelling; hydrogel; diffusion; crosslinking; network

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INTRODUCTION

A xerogel is a crosslinked polymer or copolymer, which is capable of imbibing a considerable quantity of liquid up to swelling equilibrium. With water as swelling agent, the product is termed a hydrogel [1–6].

Hydrogels are three-dimensionally crosslinked hydrophilic polymers capable of swelling and retaining possibly huge volumes of water in the swollen state. These materials are of great interest owing to their promising applications in medicine, in solving some ecological and biological problems as well as in modern technologies [7].

Hydrogels have had widespread applications in biomedicine, biotechnology, bioengineering, pharmaceutical, veterinary, food industry, agriculture and photographic technologies and other fields. Specifically, they are also used as controlled release systems of drugs, pesticides or other bioactive agents. In a controlled release system, a drug, pesticide or other bioactive agent is incorporated into a carrier, generally a polymeric material [8–12].

Crosslinked polymers with high equilibrium swelling in water or aqueous solutions can be based exclusively on macromolecules with high hydrophilicity and flexibility, often in combination with the polyelectrolyte nature of chains. Great attention has been given to the application of superabsorbent hydrogels in agriculture, soil improvement and plant growth. Superabsorbent hydrogel particles

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TABLE 1. Monomer, Crosslinkers and Agricultural Drug Used

Name	*Abbreviation*	*Formula*
Acrylamide	AAm	$H_2C{=}CHCONH_2$
Crotonic acid	CA	$CH_3CH{=}CHCOOH$
Ethylene glycol dimethacrylate	EGDMA	$(H_2C{=}C(CH_3)COOCH_2)_2$
1,4-Butandiol dimethacrylate	BDMA	$(H_2C{=}C(CH_3)COOCH_2CH_2)_2$
Sodium 2,2-dichloropropionate (Dalapon)	DAL	$CH_3C(Cl_2)COONa$

distributed in soil are capable of absorbing water; as a result this should efficiently improve the water-holding capacity of the soil and promote optimal plant growth [7].

In our previous studies, many studies about swelling of acrylamide-based hydrogels have been published. In our previous studies, adsorptions of some cationic dyes, uranyl ions and some heavy metal ions [2–4, 13–18] and protein such as bovine serum albumine [19–20] the biocompatibility of blood [21–23] by acrylamide/itaconic acid hydrogels, acrylamide/maleic acid hydrogels, and synthesis of acrylamide/crotonic acid hydrogels [24, 25] have been investigated. Inorganic salts such as ammonium sulphate, potassium nitrate and ammonium nitrate are used as fertilizers and an agricultural drug such as sodium 2,2-dichloropropionate (Dalapon) from radiation-induced acrylamide/crotonic acid hydrogels has also been investigated [26] for agricultural processing. The improper use of these contaminants by farmers causes nitrogen pollution and some toxic hazards to the environment. Much research is devoted to the controlled release of fertilizers and drugs from coated polymer matrix and hydrogels for environmental pollution control [7–10].

The aim of this study is to investigate the swelling properties of polyacrylamide hydrogels with the addition of crotonic acid which contains hydrophilic groups, some inorganic salts, two crosslinker agents and an agricultural drug. The release of fertilizers and drugs by new and novel crosslinked copolymeric hydrogels such as acrylamide/crotonic acid hydrogels may be an important application to help prevent environmental pollution. For the preparation of hydrogel systems, aqueous solutions of acrylamide, crotonic acid, some inorganic salts and two crosslinkers such as ethylene glycol dimethacrylate (EGDMA) and 1,4-butanediol dimethacrylate (BDMA) or aqueous solutions of acrylamide (AAm), crotonic acid (CA), Dalapon and crosslinkers mentioned above were irradiated by various γ-ray doses. Swelling properties, diffusional parameters and network properties of hydrogels were determined by swelling studies.

EXPERIMENTAL

Preparation of Solutions of AAm/CA Containing Salts (AAm/CA/Salt System)

To prepare highly swollen AAm/CA/salt hydrogel systems, first 1 g of AAm (BDH, Poole, UK) (Table 1) was dissolved in 1 ml of 1 M of ammonium sulfate (Merck Darmstad, Germany) or in 1 ml of 1 M of potassium nitrate (Merck Darmstad, Germany) or in 1 ml of 1 M of ammonium nitrate (Merck Darmstad, Germany) solutions and then 20 and 40 mg CA (BDH, Poole, UK) were added to the aqueous solutions of AAm/salt. To investigate the effect of crosslinkers on preparation of AAm/CA/salt hydrogel systems, 1 ml of 1% concentration of EGDMA (Merck Darmstad, Germany) or 1 ml of 1% concentration of BDMA (Merck Darmstad, Germany) was added to the aqueous solution of AAm/ammonium nitrate.

Preparation of Solutions of AAm/CA Containing Dalapon (AAm/CA/DAL)

To prepare: highly swollen AAm/CA/DAL hydrogel systems containing Dalapon (DAL), first 1 g of AAm was dissolved in 1 ml of 1 M of DAL (Sigma, St, Louis, US) solutions, and then 20 or 40 mg CA was added to the aqueous solutions of AAm/DAL. The solutions of AAm/DAL containing crosslinker were prepared as described above.

Preparation of Hydrogels by γ-Radiation

These solutions mentioned above were placed in polyvinylchloride (PVC) straws of 3 mm diameter and irradiated at 2.60 and 5.20 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, the dose rate being determined by the conventional Fricke dosimeter. Fresh hydrogels obtained in long cylindrical shapes were cut into pieces of 3–4 mm length. These were dried in air and then under vacuum, and stored for swelling studies.

The swelling of dried hydrogels was carried out by immersion in doubly distilled water at $25 \pm 0.1\,°C$ in a water bath. The water absorbed was determined by weighing the samples, after wiping, at various time intervals.

RESULTS AND DISCUSSION

A radiation technique is promising for preparation of hydrogels because a polymer in aqueous solution or in the water-swollen state readily undergoes crosslinking on irradiation to yield a gel-like material. Since this hydrogel is not contaminated with foreign additives and the crosslinking must be composed of stable C–C bonds, it is of interest to study the preparation of hydrogels by irradiation [27–29].

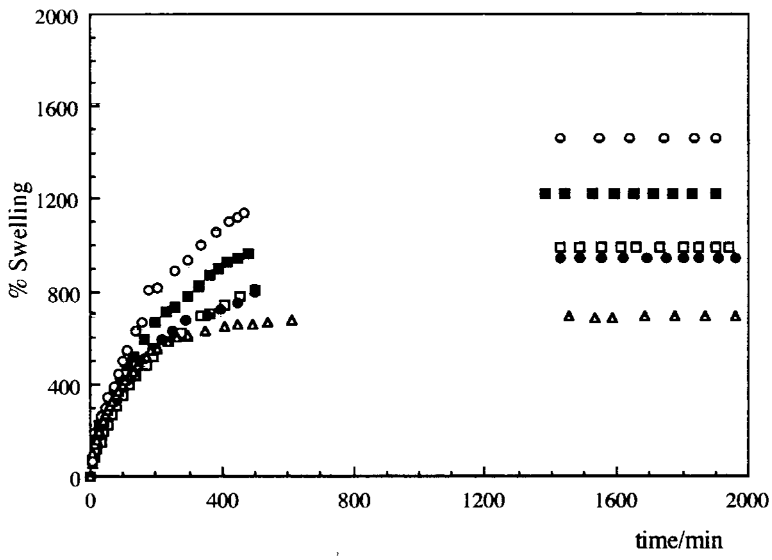

FIGURE 1. Swelling curves of AAm/CA hydrogels containing 40 mg CA and some salts. Given total dose is 5.2 kGy: △ PAAm; ○ AAm/CA; □ AAm/CA + ammonium nitrate; ■ AAm/CA + potassium nitrate; ● AAm/CA + ammonium sulphate.

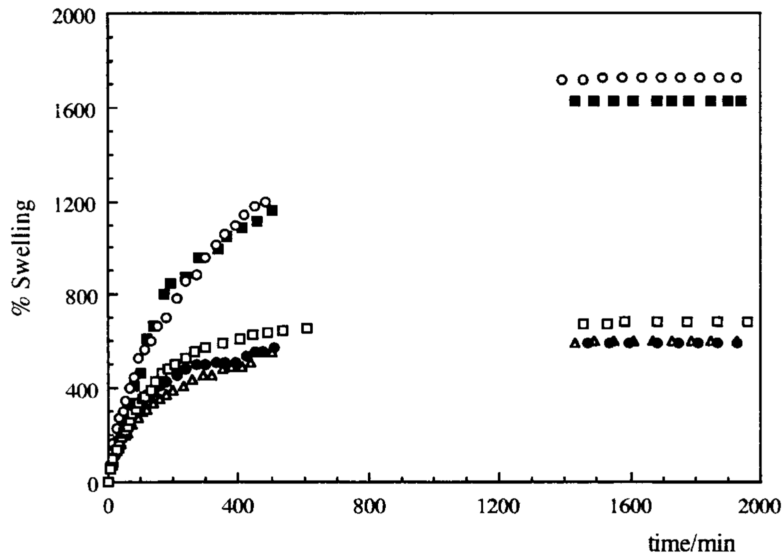

FIGURE 2. Swelling curves of AAm/CA hydrogels containing 40 mg CA, some salts and 1% crosslinking agent. Given total dose is 2.6 kGy: □ PAAm; ○ AAm/CA; ■ AAm/CA + ammonium nitrate; ● AAm/CA + BDMA + ammonium nitrate; △ AAm/CA + EGDMA + ammonium nitrate.

Preparation

In this study, ionizing radiation processing was used for the preparation of AAm hydrogels, AAm/CA hydrogels, AAm/CA/salt and AAm/CA/DAL hydrogel systems.

When monomers of acrylamide and crotonic acid in the solutions of ammonium sulfate, potassium nitrate, ammonium nitrate or DAL have been irradiated with ionization rays such as γ-rays, free radicals are generated. Random reactions of these radicals with the monomers lead to the formation of copolymers of AAm/CA. When the irradiation dose has been increased beyond a certain value the polymer chains crosslink and then a gel is obtained. Ions of salt and molecular ions of DAL are immobilized on the pores of hydrogels. Oxygen from the air is known not to affect the polymerization of acrylamide [29].

It has been reported that gelation of AAm hydrogels occurs at 2.00 kGy γ-ray irradiation doses at ambient temperature [30]. Therefore, a γ-ray dose of 2.60 kGy should be suitable for preparation of AAm, AAm/CA hydrogels, and AAm/CA/salt and AAm/CA/DAL hydrogel systems. To choose suitable conditions of the study, the results of our earlier preparation and swelling studies of crosslinked copolymeric acrylamide-based hydrogels were examined [1–5, 13–26]. After some experimental results, it was seen that suitable conditions

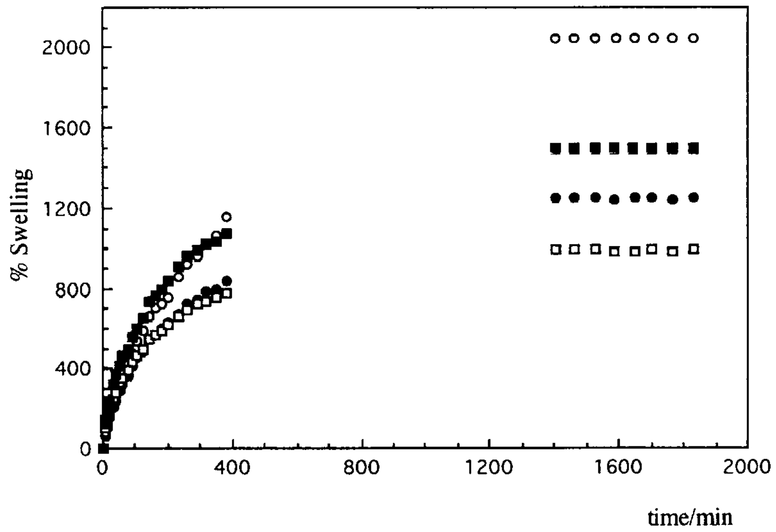

FIGURE 3. Swelling curves of AAm/CA hydrogels containing 1 M Dalapon: ■ 20 mg CA/2.6 kGy; □ 20 mg CA/5.2 kGy; ● 40 mg CA/5.2 kGy; ○ 40 mg CA/2.6 kGy.

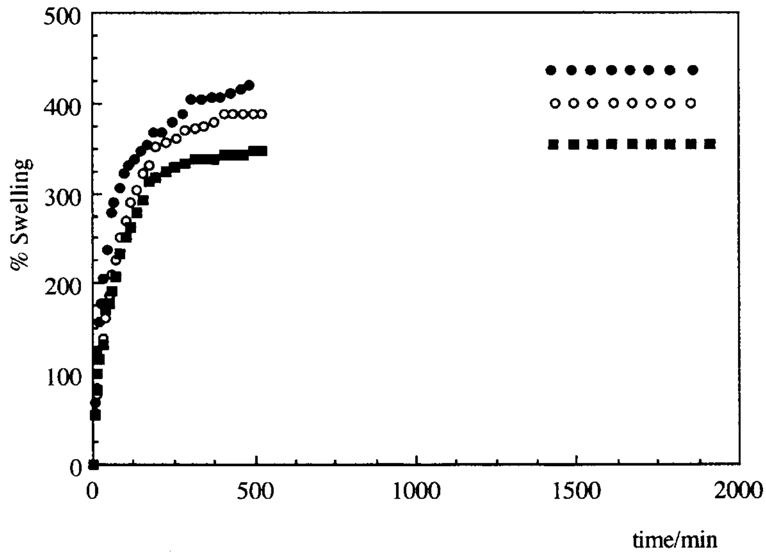

FIGURE 4. Swelling curves of AAm/CA hydrogels containing 1 M Dalapon: and 1% BDMA. Given total dose is 5.2 kGy: ● 40 mg CA; ○ 20 mg CA; ■ 0 mg CA.

for the preparation of AAm/CA hydrogel systems were 2.60 and 5.20 kGy γ-ray doses and 20 and 40 mg of CA content in 1 g of AAm. Dried gels were in the glassy form and too hard, while swollen gels were very soft. AAm/CA/salt and AAm/CA/DAL hydrogel systems are obtained in the form of cylinders. Upon swelling, the hydrogels retained their shapes.

Swelling Studies

A fundamental relationship exists between the swelling of a polymer in a solvent and the natures of the polymer and the solvent. The percentage mass swelling is the most important parameter of swelling studies. The percentage mass swelling (%S) was calculated from the following equation [1–5, 13–26, 31]:

$$\%S(m) = \frac{m_t - m_0}{m_0} \times 100 \quad (1)$$

where m_t is the mass of the swollen gel at time t and m_0 is the mass of the dry gel at time 0.

The water intake of initially dry hydrogels was followed for a long time. Swelling curves of AAm/CA/salt hydrogel systems and of AAm/CA/salt/EGDMA and AAm/CA/salt/BDMA were plotted, and representative swelling curves are shown in Figs 1 and 2. Swelling curves of AAm/CA/DAL hydrogel systems and of AAm/CA/DAL/EGDMA and AAm/CA/DAL/BDMA were plotted, and representative swelling curves are shown in Figs 3 and 4.

If Figs 1–4 are investigated together, it can be

TABLE 2. The Values of % Swelling, Diffusional Exponent and Diffusional Constant of AAm/CA Hydrogels Containing Some Salts

	PAAm	*AAm/CA*		*AAm/CA [KNO_3]*		*AAm/CA [NH_4NO_3]*		*AAm/CA [$(NH_4)_2SO_4$]*	
CA(mg)	*00*	*20*	*40*	*20*	*40*	*20*	*40*	*20*	*40*
Values of %S									
2.60 kGy	690	1840	1725	1285	1895	1415	1625	1020	1050
5.20 kGy	700	1060	1465	805	1220	960	990	720	945
Values of diffusional exponent, n									
2.60 kGy	0.64	0.66	0.62	0.62	0.63	0.67	0.78	0.61	0.59
5.20 kGy	0.53	0.82	0.68	0.57	0.60	0.65	0.63	0.57	0.55
Values of diffusional constant, $k \times 10^2$									
2.60 kGy	2.60	1.40	1.70	1.83	1.33	1.32	0.82	2.22	2.37
5.20 kGy	5.0	0.80	1.50	3.07	2.24	2.00	1.87	3.61	3.28

seen that percentage mass swelling increases with time until a certain point, when it becomes constant. This value of percentage mass swelling may be named equilibrium percentage mass swelling. The values of equilibrium percentage mass swelling of AAm/CA/salt and AAm/CA/DAL hydrogel systems were used for the calculation of some network characterization parameters. The values of percentage equilibrium mass swelling of AAm, AAm/CA, AAm/CA/salt and AAm/CA/DAL hydrogel systems are given in Tables 2–4.

Tables 2 and 3 show that the values of equilibrium percentage mass swelling of AAm range between 690 and 700%, but the values of equilibrium percentages swelling of AAm/CA hydrogels vary between 1060 and 1840% for AAm/CA hydrogels. The values of equilibrium volume swelling of AAm/CA/salt hydrogel sys-

TABLE 3. The Values of % Swelling, Diffusional Exponent, Diffusional Constant, Diffusion Coefficient [D (cm²/sec) $\times 10^6$] and Intrinsic Diffusion Coefficient [$\mathcal{D}$ (cm²/sec) $\times 10^6$] of AAm/CA hydrogels containing 1 M DAL

	Mass of acid			
	20 mg CA		*40 mg CA*	
Dose	*2.6 kGy*	*5.2 kGy*	*2.6 kGy*	*5.2 kGy*
%S	1490	985	2045	1245
$k \times 10^2$	3.64	3.80	1.38	1.98
n	0.52	0.54	0.63	0.62
$D \times 10^6$	1.76	2.68	1.17	1.91
$\mathcal{D} \times 10^6$	2.51	3.84	2.50	3.45

TABLE 4. The Values of % Swelling, Diffusional Exponent, Diffusional Constant, Diffusion Coefficient (D (cm²/sec) $\times 10^6$) and Intrinsic Diffusion Coefficient ($\mathcal{D}$ (cm²/sec) $\times 10^6$) of AAm/CA Hydrogels Containing Crosslinkers, Salts and DAL

	1% EGDMA						*1% BDMA*					
Dose	*2.6 kGy*			*5.2 kGy*			*2.6 kGy*			*5.2 kGy*		
CA /mg	*00*	*20*	*40*	*00*	*20*	*40*	*00*	*20*	*40*	*00*	*20*	*40*
1 M ammonium nitrate												
%S	500	540	610	440	540	575	395	450	595	375	435	450
n	0.51	0.56	0.55	0.54	0.56	0.52	0.50	0.47	0.59	0.55	0.47	0.51
$k \times 10^2$	5.95	3.76	3.63	5.51	4.19	4.43	6.81	6.27	3.86	6.08	7.21	6.10
$D \times 10^6$	3.07	1.88	1.74	3.19	2.17	2.26	4.05	2.44	2.81	3.92	2.71	2.95
$\mathcal{D} \times 10^6$	3.64	2.49	2.31	3.82	2.79	2.91	4.80	3.07	3.47	4.55	3.34	3.61
1 M DAL												
%S	395	491	512	330	467	495	378	430	474	354	400	437
n	0.56	0.52	0.53	0.58	0.56	0.50	0.62	0.59	0.54	0.50	0.53	0.62
$k \times 10^2$	6.03	5.81	5.69	6.54	5.65	6.76	5.14	5.51	6.78	7.14	5.97	5.45
$D \times 10^6$	2.60	2.83	3.02	3.48	2.51	3.26	3.63	4.12	3.60	3.92	3.68	5.41
$\mathcal{D} \times 10^6$	2.93	3.34	3.42	3.85	2.85	3.82	4.01	4.93	4.13	4.46	4.24	6.14

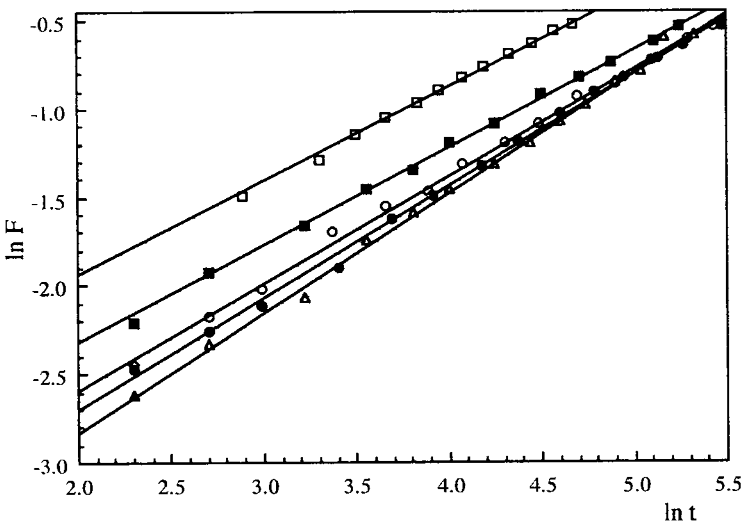

FIGURE 5. Kinetic curves of AAm/CA hydrogels containing 40 mg CA and some salts. Given total dose is 5.2 kGy: △ PAAm; ○ AAm/CA; □ AAm/CA + ammonium nitrate; ■ AAm/CA + potassium nitrate; ● AAm/CA + ammonium sulphate.

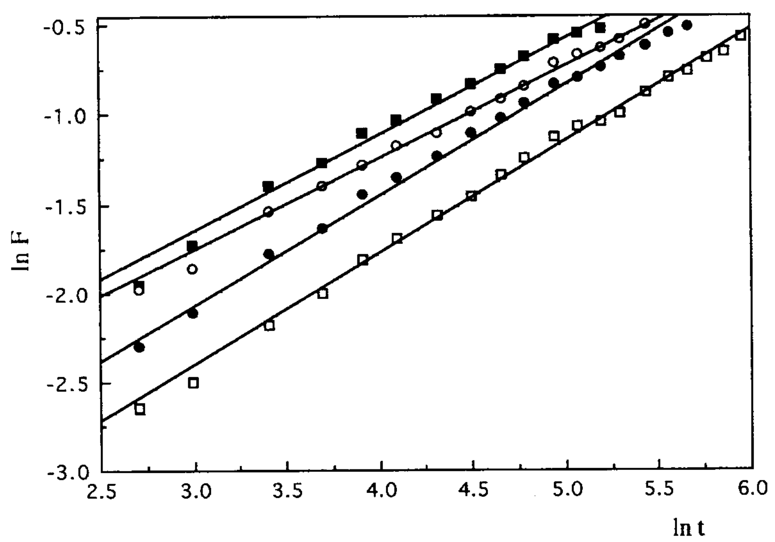

FIGURE 6. Kinetic curves of AAm/CA hydrogels containing 1 M Dalapon; ○ 20 mg KA/2.6 kGy; □ 40 mg KA/2.6 kGy; ■ 20 mg KA/5.2 kGy; ● 40 mg KA/5.2 kGy.

tems vary between 720 and 1890% and 985 and 2045% for AAm/CA/DAL systems.

The hydrophilic group numbers of AAm/CA copolymers are more than those of acrylamide, so the swelling of AAm/CA copolymers is greater than that of acrylamide copolymers. On the other hand, when the irradiation dose was increased, the equilibrium mass swelling degree of AAm/CA copolymers decreased. When the content of CA in AAm/CA copolymers increased, the equilibrium percentage swelling of AAm/CA copolymers increased. Furthermore, as said before, the equilibrium percentage swelling of AAm is lower than that of AAm/CA copolymers. The reason for this is the existence of hydrophilic groups on the crotonic acid causing a greater degree of swelling on AAm/CA copolymeric hydrogels.

When the irradiation dose was increased, the number of the small chains increased at unit copolymerization time and the crosslink density of AAm/CA Copolymeric system was higher than for lower irradiation doses.

The effect of salt ions and DAL is important to swelling of AAm-based hydrogels. There are many ions containing oxygen on the salts and many molecular 2,2-dichloropropionate ions. These unpaired electrons on oxygen atoms are centres for new hydrogen bonding sites as the hydrophilic group. For these reasons, the equilibrium percentage mass swelling of AAm/CA/salt and AAm/CA/DAL is bigger than for AAm hydrogels.

The effect of crosslinker can be seen in Figs 2 and 4. There is a decrease in the swelling ratio because the molecules of the crosslinkers are placed between the chains of AAm and CA. Then the hydrophilic group number and the swelling ratio

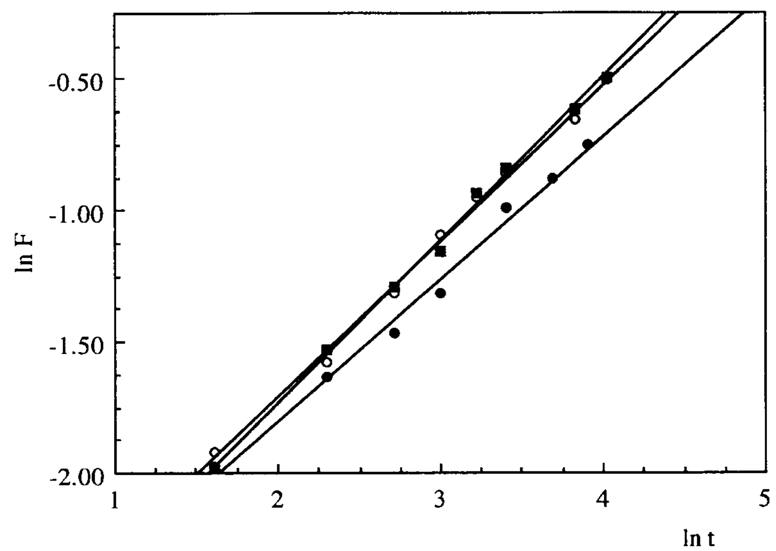

FIGURE 7. Kinetic curves of AAm/CA hydrogels containing 1 M Dalapon and 1% BDMA. Given total dose is 2.6 kGy: ● 40 mg CA; ○ 20 mg CA; ■ 10 mg CA.

decrease. The more crosslinker molecules there are in the hydrogel, the lower the swelling ratio in AAm/CA/salt and AAm/CA/DAL hydrogel systems [25].

Diffusion

When a glassy hydrogel is brought into contact with water, water diffuses into the hydrogel and the hydrogel swells. Diffusion involves migration of water into pre-existing or dynamically formed spaces between hydrogel chains. Swelling of the hydrogel involves larger-scale segmental motion resulting, ultimately, in an increased distance of separation between hydrogel chains [32].

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

The following equation was used to determine the nature of diffusion of water into hydrogels [1–5, 13–26]:

$$F = M_t/M_\infty = kt^n \tag{2}$$

whereM_t and M_∞ denote the amount of solvent diffused into the gel at time t and infinity (at equilibrium) respectively, k is a constant related to the structure of the network, and the exponent n is a number to determine the type of diffusion. For cylindrical shapes, $n = 0.45–0.50$ and corresponds to Fickian diffusion whereas $0.50 < n < 1.0$ indicates that diffusion is nonFickian. This equation is applied to the initial stages of swelling and plots of ln F versus ln t yield straight lines up to almost 60% increase in the mass of hydrogel [31].

For the hydrogels, ln F versus ln t plots were drawn using the kinetics of swelling and some representative results are shown in Figs 5–7.

The exponents n were calculated from the slopes of the lines and are listed in Tables 2–4, where it is shown that the values of the diffusional exponent range generally between 0.50 and 0.70. In the experiments, the number to determine the type of diffusion (n) was found to be generally over 0.50.

TABLE 5. The Values of Diffusion Coefficient (D (cm^2/sec) $\times 10^6$) and Intrinsic Diffusion Coefficient [$\mathcal{D}$ (cm^2/sec) $\times 10^6$] of AAm/CA Hydrogels Containing Some Salts

	PAAm	*AAm/CA*		*AAm/CA [KNO_3]*		*AAm/CA [NH_4NO_3]*		*AAm/CA [$(NH_4)_2SO_4$]*	
CA/(mg)	*00*	*20*	*40*	*20*	*40*	*20*	*40*	*20*	*40*
(D (cm^2/sec) $\times 10^6$)									
2.60 kGy	2.79	1.55	2.25	1.24	1.42	1.46	1.97	2.02	1.94
5.20 kGy	3.39	3.58	2.93	2.22	2.13	2.56	2.08	2.32	2.30
($\mathcal{D}$ (cm^2/sec) $\times 10^6$)									
2.60 kGy	3.22	2.49	3.51	1.99	3.66	2.61	4.01	2.83	3.13
5.20 kGy	3.82	4.83	4.05	3.06	3.21	3.75	3.10	3.01	3.30

TABLE 6. The Values of Average Molar Mass (M_c), Crosslink Density (q) and Number of Elastically Effective Chains (v_e) of AAm/CA Hydrogels Containing Salts

	PAAm	AAm/CA		AAm/CA [KNO_3]		AAm/CA [NH_4NO_3]		AAm/CA [$(NH_4)_2SO_4$]	
CA / mg	00	20	40	20	40	20	40	20	40
M_c									
2.60 kGy	17,900	239,000	204,000	96,400	257,900	123,500	174,800	52,300	56,500
5.20 kGy	18,600	58,000	134,000	27,700	83,700	44,600	48,700	20,600	42,800
$q \times 10^4$									
2.60 kGy	39.7	9.4	3.4	7.4	2.7	5.8	4.1	13.6	12.7
5.20 kGy	38.0	10.7	7.0	25.8	8.6	16.0	14.7	34.6	16.7
$v_e \times 10^{-18}$									
2.60 kGy	43.8	10.3	3.7	8.1	3.1	6.4	4.5	14.9	13.8
5.20 kGy	41.9	11.7	7.7	28.3	9.4	17.5	16.1	38.0	18.3

TABLE 7. The Values of Average Molar Mass (M_c), Crosslink Density (q) and Number of Elastically Effective Chains (v_e) of AAm/CA Hydrogels Containing 1% Crosslinkers

	1% EGDMA						1% BDMA					
Dose	2.6 kGy			5.2 kGy			2.6 kGy			5.2 kGy		
CA/ mg	00	20	40	00	20	40	00	20	40	00	20	40
1 M ammonium nitrate												
M_c	7420	9340	12,770	5050	9220	11,000	3710	6790	12,130	3280	5000	5430
$q \times 10^4$	97.6	77.8	57.5	143.4	78.8	66.3	195.9	107.5	60.2	221.2	145.8	134.7
$v_e \times 10^{-18}$	105.7	83.9	61.4	155.2	85.0	71.3	211.4	115.5	64.6	238.7	156.8	144.3
1 M DAL												
M_c	3767	7041	7956	2215	6095	7219	3306	4806	6161	2734	3907	5043
$q \times 10^4$	192.1	103.2	916.5	326.8	119.2	101.0	219.7	151.7	118.7	265.7	186.6	145.0
$v_e \times 10^{-18}$	208.0	111.3	98.51	353.8	128.5	108.6	237.0	163.0	127.2	286.6	200.6	155.4

Hence the diffusion of water into AAm, AAm/CA, AAm/CA/salt and AAm/CA/DAL hydrogel systems had a *nonFickian* character [31]. In this diffusion, diffusion and relaxation are said to be isochronal effective [31].

The study of diffusion phenomena in hydrogels and water is of value in that it clarifies polymer behavior. The complete swelling–time curves for hydrogels in water are used to calculated diffusion coefficient and intrinsic diffusion coefficient [33]. The percentage mass swelling parameters were used to calculate the diffusion coefficient and the intrinsic diffusion coefficient. In hydrogel characterization, diffusion coefficients were calculated from the following equations:

$$D = \frac{0.049}{(t/4l^2)_{1/2}} \qquad (3)$$

where D in cm^2/sec, t is the time at which the swelling is one half the equilibrium value ($V/V_0 = 1/2$) and l is the radius of the cylindrical polymer sample. The intrinsic diffusion coefficient may be expressed as:

$$\mathscr{D} = D(1 - V)^{-3} \qquad (4)$$

where V is volume fraction of solvent penetrating the polymer by the time t defined above [33].

The values of the diffusion coefficient and intrinsic diffusion coefficient of AAm, AAm/CA AAm/CA/salt, AAm/CA/ammonium nitrate/EGDMA–BDMA, AAm/CA/DAL and AAm/CA/DAL/EGDMA–BDMA hydrogel systems are listed in Tables 3–5.

Tables 3–5 show that the values of the intrinsic diffusion coefficient of the hydrogel systems are higher than the values of their diffusion coefficient. This is because eq. (3) gives a measure not only of diffusion but also of the mass flow of the whole system. Equation 4 gives the intrinsic diffusion coefficient for cases where no mass action effects enter [33].

Network studies

One of the important structural parameters characterizing crosslinked polymers is M_c, the average molar mass between crosslinks, which is directly related to the crosslink density. The magnitude of M_c significantly affects the physical and mechanical properties of crosslinked polymers and its determination has great practical significance. Equilibrium swelling is widely used for the

TABLE 8. The Values of Average Molar Mass (M_c), Crosslink Density (q) and Number of Elastically Effective Chains (v_e) of AAm/CA Hydrogels Containing 1 M DAL

	Mass of acid			
	20 mg CA		40 mg CA	
Dose (kGy)	2.6	5.2	2.6	5.2
M_c	141,550	47,970	312,590	88,350
$q \times 10^4$	5.04	14.87	2.29	8.11
$v_e \times 10^{-18}$	5.54	16.34	2.50	8.87

determination of M_c. Early research by Flory and Rehner laid the foundations for the analysis of equilibrium swelling. According to the theory of Flory and Rehner, the following equation could be obtained for a perfect network:

$$M_c = -V_1 d_p \frac{(v_s^{1/3} - v_s/2)}{\ln(1 - v_s) + \chi v_s^2 + v_s} \qquad (5)$$

where M_c is the number-average molar mass of the chain between crosslinks; V_1 is the molar volume (ml/g); d_p is the polymer density (g/ml); v_s is the volume fraction of polymer in the swollen gel; χ is the Flory–Huggins interaction parameter between solvent and polymer [34].

The swelling ratio (Q) is equal to $1/v_s$. Here, the crosslink density, q, is defined as the mole fraction of crosslinked units [34]:

$$q = M_0/M_c \qquad (6)$$

where M_0 is the molar mass of the repeating unit.

Other authors define a crosslink density, v_e, as the number of elastically effective chains, totally included in a perfect network, per unit volume. v_e is simply related to q:

$$v_e = d_p N/M_c \qquad (7)$$

where N is the Avogadro number. Then

$$v_e = d_p N q/M_0 \qquad (8)$$

The values of V_1, d_p and χ were taken from related literature [25]. The number-average molar mass between crosslinks, the crosslink density and the number of elastically effective chains of AAm, AAm/CA AAm/CA/salt, AAm/CA/ammonium nitrate/EGDMA–BDMA, AAm/CA/DAL and AAm/CA/DAL/EGDMA–BDMA hydrogel systems were calculated and listed in Tables 6–8.

Table 6, shows that the number-average molar mass between crosslinks of hydrogels increased with increasing CA content of AAm/CA hydrogels while they decreased with increasing irradiation dose. Because CA in hydrogels has included many hydrophilic groups, AAm/CA hydrogels have swollen greatly. The values of the crosslink density and the number of elastically effective chains are related owing to the value of the number-average molar mass between crosslinks (Tables 7 and 8). Similar behavior was observed on the network properties of AAm/CA/salt, AAm/CA/ammonium nitrate/EGDMA–BDMA, AAm/CA/DAL and AAm/CA/DAL/EGDMA–BDMA hydrogel systems

CONCLUSION

In this study, the swelling properties and some parameters about diffusion and network studies of AAm/CA/salt and AAm/CA/DAL hydrogel systems were investigated. The main aim of this investigation was to obtain preliminary swelling properties of AAm/CA/salt and AAm/CA/DAL hydrogel systems, for probable controlled release of inorganic salts and DAL from crosslinked copolymeric hydrogel systems.

Crosslinked AAm/CA copolymers may be used for this purpose. In this study, it was shown how acrylamide, crotonic acid and two crosslinkers, such as ethylene glycol dimethacrylate and 1,4-butandiol dimethacrylate, in some aqueous solutions of inorganic salts such as ammonium sulfate, potassium nitrate and ammonium nitrate and an agricultural drug such as Dalapon (sodium 2,2-dichloropropionate) were used for copolymerization of acrylamide/crotonic acid hydrogel systems by using γ-rays.

At present, one of the problems of environmental pollution concerns water and waste-water, and improper use of fertilizers and agricultural drugs causing pollution by nitrite, nitrate, phosphate and organic substance pollution. For this purpose, coated polymer matrixes and polymeric and copolymeric hydrogel systems will be useful for the controlled release of fertilizers and pesticides.

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