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A. K. Bajpai^a; Anjali Giri^a

^a Department of Chemistry, Bose Memorial Research Laboratory, Government Autonomous Science College, Jabalpur, India

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**SWELLING DYNAMICS OF A TERNARY
INTERPENETRATING POLYMER NETWORK
(IPN) AND CONTROLLED RELEASE OF
POTASSIUM NITRATE AS A MODEL
AGROCHEMICAL**

A. K. Bajpai* and Anjali Giri

Bose Memorial Research Laboratory, Department of Chemistry,
Government Autonomous Science College, Jabalpur 482 001, India

ABSTRACT

An interpenetrating polymer network (IPN) of carboxymethyl cellulose (CMC), polyethylene glycol (PEG) and crosslinked polyacrylamide (PAM) has been prepared and dynamic water sorption properties have been investigated as a function of chemical architecture of the IPN, pH and temperature of the swelling medium and presence of salt ions in the bathing medium. Based on the Fick's law the swelling exponent (n) and diffusion constant (D) were evaluated suggesting possible modes of water transport through the IPN's. The IPN's synthesized were loaded with KNO_3 as a representative agrochemical and its release dynamics was studied conductometrically. The influences of percent loading and chemical composition of the IPN were also observed on the release rate and released amounts of KNO_3 .

*Corresponding author.

INTRODUCTION

Macromolecular formulations like the graft, random and block copolymers [1], interpenetrating polymer networks [2], and hydrogels [3] are currently the focus of considerable scientific research due to their potential for application in a large variety of areas such as medicine, industry, environmental clean-up, and agriculture. The reason for this vast potential is not only due to their ability to respond reversibly to external stimuli such as pH [4], temperature [5], ionic strength [6], electric field [7], etc., but also their capacity to act as a carrier of a variety of bioactive compounds like proteins [8], low and high molecular weight drugs [9]. Such loaded polymeric carriers swell and subsequently deliver the entrapped compounds into the aqueous reservoirs when allowed to contact a still release medium. This process forms the very foundation of the drug delivery technology, which has been an active area of research in agriculture in recent past. Controlled release polymer matrix systems offer a number of potential advantages over the conventional means of applications [10]. The principal advantage is that these systems allow much less active agent to be used for the desired of activity [11].

Agrochemicals are bioactive agents concerned with the utilization of chemicals to improve production of crops for a plentiful and high quality food supply for consumers. Hence, a great increase in the quantities of these chemicals is necessary for enhancing any substantial increase in farm production of food stuffs. However, considering the present method of food-stuffs, one cannot increase both farm output and ensure a high quality environment [12]. Depending on the method of application and on the climatic conditions as much as 90% of conventionally applied agrochemicals never reach their objectives, to produce the desirable biological response at the present time and in the quantities required [20].

Conventional applications of agrochemicals results in ground water contamination which becomes a serious issue [13]. Also, over application and point source contamination increase the pollution potential, this leads to unnecessary spreading of toxic substances in the environment by leaching or is run off by rainfall irrigation to ground water and volatilization, as well as by human factors such as excessive application, spills, and improper disposal. This may also result in potential hazards to non-target organisms by direction action or, for instance, by residues in food [14].

One of the most alarming problems is that three fourths of the world population living in developing countries is facing the nitrate leaching and subsequent pollution of ground water [15]. Due to increased agricultural activity, which is necessary for enhanced food production, and also due to industrial activity, there is an increasing evidence of nitrate pollution of ground waters. What actually happens is that the excess nitrates leach down the soil profile with percolating water. The seriousness of the problem can be assessed by the fact that nitrates and nitrites may result in many fatal



physiological disorders such as methemoglobinemia in babies [16], oral cancer [17], cancer of the colon, rectum or other gastrointestinal cancers [18], Alzheimer's disease [19], etc. Craig et al. [20] have shown that nitrate consumption leads to a decrease in the ascorbate/nitrite ratio in gastric juice, which regulates the synthesis of potentially carcinogenic N-nitroso compounds and decrease in the ratio leads to increased risk of gastric cancer.

Treatment of ground water for the removal of nitrates or prevention of nitrate from reaching ground water is possible. Chemical methods such as catalytic removal of nitrate from water [21], abiotic degradation of nitrates using zerovalent iron and electrokinetic processes [22], biotechnological methods [23], and physical methods such as reverse osmosis and nano-filtration [24] have been reported. These processes are at present considered costly even in advanced countries [25]. Thus, at this situation the application of a nitrate loaded carrier with a swelling controlled release property could be proved to be a suitable technology against nitrate pollution of groundwaters.

Various studies have been carried out to control the release of pesticides and pharmaceuticals to achieve the desired results over a prescribed duration [26]. Biodegradable matrices are especially preferred in pesticide formulations in order to prevent a different kind of pollution created by residues of depleted, non degradable pesticide carriers. Sodium carboxymethyl cellulose (CMC) can be converted into a hydrogel with ease via chelation with polyvalent cations [27]. It also possesses the advantages of being biodegradable, hydrophilic and economic. It was, therefore, aimed at constructing a swellable controlled release system comprising of CMC, polyethylene glycol (PEG) and crosslinked polyacrylamide (PAM) chains entangled into one another via physical interactions and thus resulting in a highly hydrophilic and water insoluble macromolecular network. The use of PEG as one of the components of hydrogel not only provides hydrophilicity to the network but also insolubilizes the CMC chains by building up H-bands with them.

EXPERIMENTAL

Carboxymethyl cellulose sodium salt (CMC) was obtained from Loba Chemie, India and used as received. Polyethylene glycol (PEG) was a liquid of low mol. wt. (600) supplied by Research Lab, Pune, India and used without any pretreatment. Acrylamide (Loba Chemie, India) was freed from the inhibitor by usual crystallization method and dried in vacuum for a week. The crosslinking agent employed was N,N'-methylene bis acrylamide (MBA) obtained from Central Drug House, Lucknow, India and used as received. Other required chemicals were of analytical reagent grade and doubly distilled water was used throughout the study.



Method

Preparation of Hydrogel

The hydrogel was prepared by a free radical polymerization method as described in our earlier communications also [28]. In a typical experiment, CMC 2.0% v/v, PEG 7.5% v/v, AM 3.75% w/v, MBA 0.05% w/v and potassium persulphate 0.05% w/v were added into a petri-dish (2 inch diameter, Corning). The whole mixture was homogenized and put into an oven for 3 hours at 80°C so that the fluid converted into a thick semi-transparent mass. The gel that formed was dried overnight at 60°C so that it changed into a thin circular film. The hydrogel film was freed from the unreacted chemicals by equilibrating it with distilled water for 15 days and then drying it at room temperature. The dry gel film was cut into nearly Identical sized pieces and stored in polyethylene bags.

Swelling Kinetics

The progress of the swelling process was monitored by a conventional gravimetric procedure. In brief, a preweighed piece of hydrogel (0.1 g) was placed in an aqueous reservoir and allowed to swell for a definite time period. The swollen piece was taken out at predetermined time intervals, pressed in between the two filter papers to remove excess water and finally weighed in a sensitive analytical balance. The swelling ratio was calculated by the following relation:

$$\text{Swelling Ratio} = \frac{\text{Weight of the swollen gel}}{\text{Weight of the dry gel}} \quad (1)$$

The kinetic swelling data was analyzed by the following equation [29]:

$$\frac{W_t}{W_\infty} = k t^n \quad (2)$$

where k is the swelling rate front factor and n is the swelling exponent; and W_t and W_∞ the water intakes at time t and equilibrium time respectively. The above equation is a phenomenologically rate law where the swelling exponent n provides insights into the type of water sorption mechanism that is operative. For instance, ($n = 0.5$ shows a Fickian kinetics in which the sorption is diffusion controlled while the value of n between 0.5 and 1.0 indicates a non-Fickian process (or Case II transport) where chain relaxation also contributes to water sorption process.



The diffusion constants D of water through the hydrogel were calculated according to the following equation [30]:

$$\frac{W_t}{W_\infty} = 4 \left[\frac{Dt^2}{\pi l^2} \right]^2 \quad (3)$$

where l is the thickness of the hydrogel.

Release Study

Loading of Potassium Nitrate

The loading of a hydrogel is normally done by two methods. In the first method, the compound to be loaded is mixed with the reaction mixture prior to polymerization and then the hydrogel matrix is prepared by polymerizing the monomer(s). The bioactive compound is entrapped within the gel matrix [31]. In the second approach, the dry gel (xerogel) is allowed to swell in the bioactive compound solution and after the equilibrium swelling the gel is dried and the device is obtained [32]. The later method has some advantages over the first one as polymerization could have an adverse effect on the activity of the entrapped compound and this purification of the device remains a problem.

In the present study, the second method was followed by swelling of dry gel in a known solution of KNO_3 . The swollen gels were dried and stored properly. The % loading was calculated by the following equation:

$$\% \text{ loading} = \frac{\text{Amount of } \text{KNO}_3 \text{ loaded}}{\text{Weight of unloaded gel}} \times 100 \quad (4)$$

Examination of Released KNO_3

In a typical release experiment, a KNO_3 loaded gel of known weight and % loading was placed into 25 mL distilled water as a release medium under unstirred conditions. The amount of released KNO_3 was estimated by measuring the conductivity of the release medium by a conductivity meter (Systronics, Model No. 303, India) and knowing the amount of released KNO_3 with the help of a calibration plot. Similarly, the equilibrium amount of released KNO_3 (M_∞) was determined by measuring the conductivity of the release medium after 12 days. The release data was analyzed kinetically by Eqs. (2) and (3), and the diffusional exponent (n) and diffusion constant of KNO_3 (D) were evaluated graphically.



RESULTS AND DISCUSSION

Dynamic Model for Swelling Release

A loaded hydrogel could be pictured as a network of macromolecular chains bonded to one another via physical or chemical forces containing patches of free volumes in between them. These free volumes of varying mesh sizes are further occupied by the active agent. In the present study, the macromolecular chains of PEG, CMC and PAM constitute a hydrogel network within that the molecules of potassium nitrate are entrapped in the loaded hydrogel. When the loaded hydrogel is allowed to contact a still aqueous release medium, the penetrant water molecules invade the hydrogel surface and a moving solvent front is observed that clearly separates the unsolvated glassy polymer region ahead of the front from the swollen and rubbery gel phase behind it [33] (Fig. 1). Just ahead of the front, the presence of solvent plasticizes the polymer and causes it to undergo a glass to rubber transition [34]. Now the following possibilities arise:

1. If the glass transition temperature of the polymer (T_g) is well below the experimental temperature, the polymer will be in the rubbery

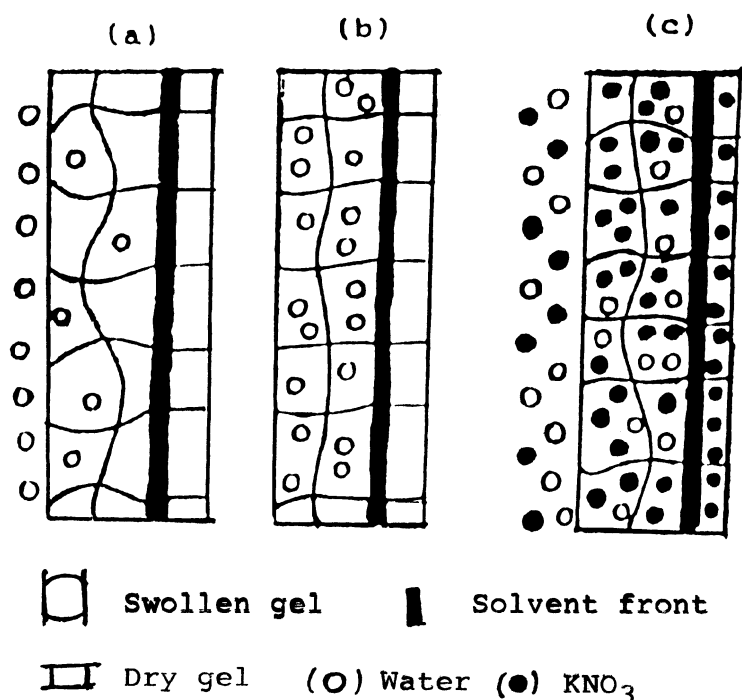


Figure 1. A model depicting the dynamic water-sorption mechanisms (a) Fickian; (b) Non-Fickian; (c) Release of KNO_3 .

state and polymer chains will have a higher mobility that allows an easier penetration of the solvent [35]. This clearly results in a Fickian diffusion (Case I) which is characterized by a solvent diffusion rate, R_{diff} , slower than the polymer relaxation rate, R_{relax} ($R_{diff} \ll R_{relax}$). The whole mechanism is modeled in Fig. 1(a).

As soon as the water molecules diffuse into the pockets of the hydrogel, the entrapped potassium nitrate molecules diffuse out into the bulk of the release medium. Obviously, a Fickian release will be observed when the rate of diffusion of potassium nitrate is slower than that of the relaxation of macromolecular chains. The above swelling or release situations are indicated by a 0.5 value of the swelling (or diffusional) exponent 'n' of Eq. (2).

2. If the experimental temperature is below T_g , the polymer chains are not sufficiently mobile to permit immediate penetration of the solvent (or release of the active agent) into the polymer core. This gives rise to a non Fickian diffusion process depending on the relative rates of diffusion and chain relaxation (For Case II, $R_{diff} \gg R_{relax}$ and for anomalous, $R_{diff} \sim R_{relax}$).

Both the possibilities are depicted in Figs. 1(a) and 1 (b), respectively. Figure 1(c) represents a release mechanism of of KNO_3 .

Effect of Hydrogel Composition on Swelling

A hydrogel, in general, is made up of hydrophilic (and/or hydrophobic) components and a suitable crosslinking agent. Apart from the chemical functions of the hydrogel, the swelling of a hydrogel network is also regulated by the physical force and subsequent elastic responses of the constituent macromolecular chains of the matrix. According to Flory's swelling theory [36], the following Equation can be given:

$$Q^{5/3} = \left\{ \left[\left(\frac{i}{2V_N} \cdot S^{1/2} \right)^{1/2} + (1/2 - X_1)/V_1 \right] / (v_e/V_o) \right\} \quad (5)$$

where i/V_N is the concentration of the fixed charge referred to unswollen network, S is the ionic concentration in the external solution, $(1/2 - X_1)/V_1$ is the affinity of the hydrogel for water, and v_e/V_o is the crosslinked density of the hydrogel. The above equation reveals that the swelling ratio has direct relation to ionic osmotic pressure, crosslinked density and the affinity of the hydrogel for water. Thus, varying the composition of the hydrogel has a direct control over swelling.

PEG, a hydrophilic polymer, exhibits great affinity towards water molecules. The nature of the association of water with PEGs containing terminal hydroxyl groups and poly(ethylene oxide) units has been an active area of research in recent past. It has been shown from various thermal



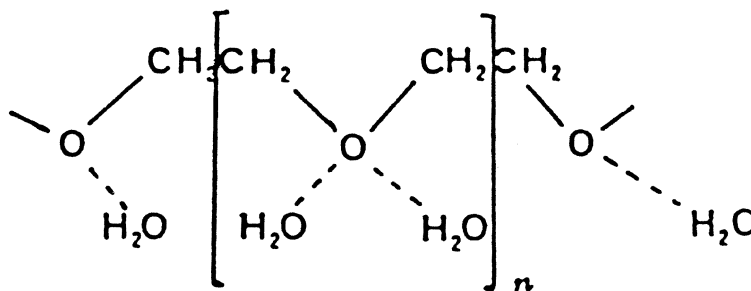


Figure 2. Formation of dihydrates by poly(ethylene glycol) (PEG).

measurements that the PEG could give rise to formation of dihydrates via H-bond formation as depicted in Fig. 2. When the concentration of PEG is increased in the feed mixture in the range 2.5 to 10.0% v/v, the swelling ratio constantly increases as shown in Fig. 3. The observed increase may be explained by the fact that with increasing PEG content in the gel, the hydrophilicity of the network will also increase and as predicted by the Flory's equation the swelling ratio increases.

Carboxymethyl cellulose (CMC) being a modified natural water soluble polymer (Fig. 4) contains hydroxyls and carboxyl groups which impart hydrophilicity to the molecule. When the concentration of CMC is increased in the feed mixture of the IPN in the range 0.5 to 2.0% w/v, the swelling ratio is found to increase substantially as shown in Fig. 5. The observed large swelling ratio can be explained by the fact that increased CMC content in the IPN renders the network more hydrophilic and, therefore, the degree of water sorption increases. What actually happens is that as soon as the polymer matrix contacts the dissolution medium, such as water, the molecules of water penetrates the gel and swells the macromolecular chains. Molecularly, individual chains, originally found in their unperturbed state, absorb water so that their end-to-end distance and radius of gyration expand to the new solvated state.

When the concentration of acrylamide is increased in the feed mixture in the range 2.5 to 7.5% w/v the swelling ratio is found to decrease (Fig. 6) constantly in the whole range of monomer. The observed decrease has been frequently noticed [37] and can be explained by the fact that increased monomer concentration results in a greater number of crosslinked PAM chains which in turn increases the crosslinked density of the IPN and, therefore, brings about a fall in the swelling ratio.

An effective way of modifying water-sorption characteristics of a hydrogel is to vary the concentration of the crosslinker in the feed mixture of the gel. This effectively affects the elastic response of the macromolecular matrix which apart from free energies of mixing of polymer chains and solvent is also a decisive factor in regulating the swelling process. In the present



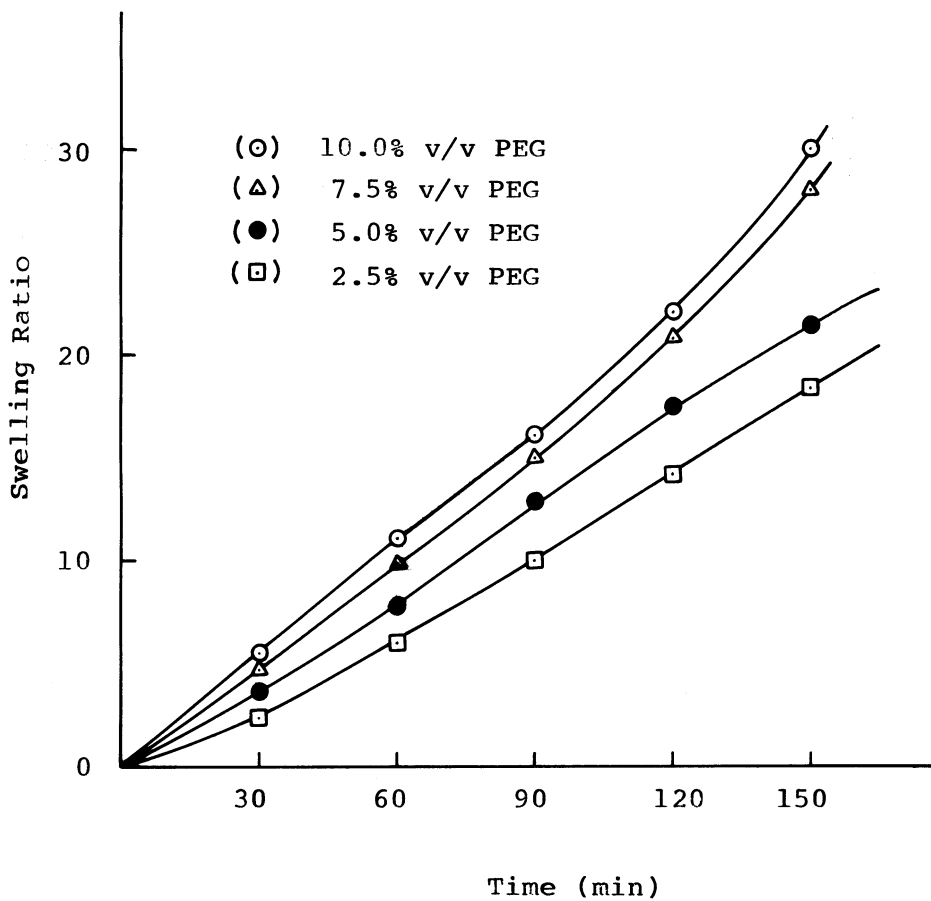


Figure 3. Effect of variation in PEG content of the IPN's on their swelling ratio. [CMC]=2.0% w/v, [AM]=3.75% w/v, [MBA]=0.05% w/v, Temp.=27°C.

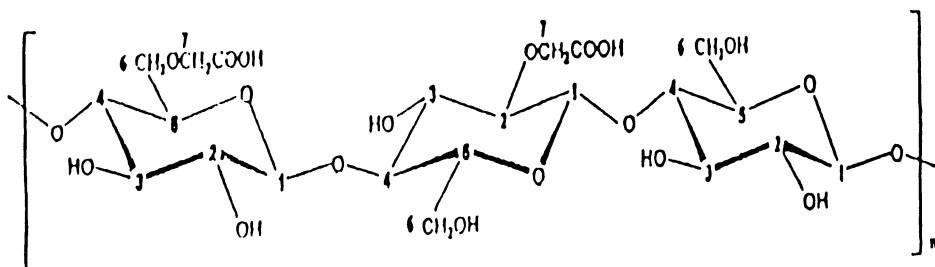


Figure 4. Structure of carboxymethyl cellulose (CMC).

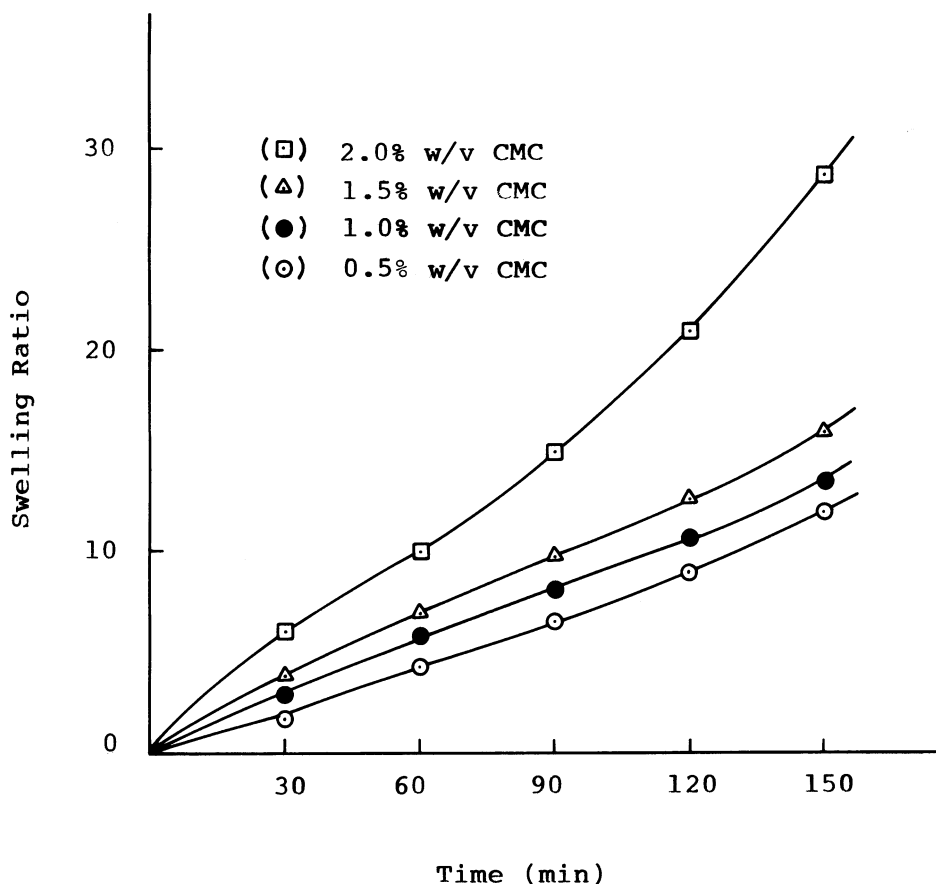


Figure 5. Effect of variation in CMC content of the IPN's on their swelling ratio. [PEG] = 7.5% w/v, [AM] = 3.75% w/v, [MBA] = 0.05% w/v, Temp. = 27°C.

study the concentration of crosslinker (MBA) has been varied in the range 0.05 to 0.30% w/v and the results are depicted in Fig. 7. The results clearly reveal that with increasing crosslinker concentration the swelling ratio substantially decreases. The results are quite usual and can be explained by the fact that with increasing crosslinking density the mesh size, i.e., the space between the macromolecular chains, decreases which restricts the penetration of solvent molecules into the IPN thus causing a fall in the swelling ratio. Some workers [38] have observed an increase in the glass transition temperature of the hydrogel (T_g) with increasing crosslinker concentration and attributed the increased T_g to the decrease in the swelling ratio.

Another cause for the observed decrease in swelling ratio may be that due to increasing amounts of crosslinker in the gel, the crosslinked density increases which shortens the average molecular weight of the polymer between two crosslink points and thus reduces the mesh sizes of the free

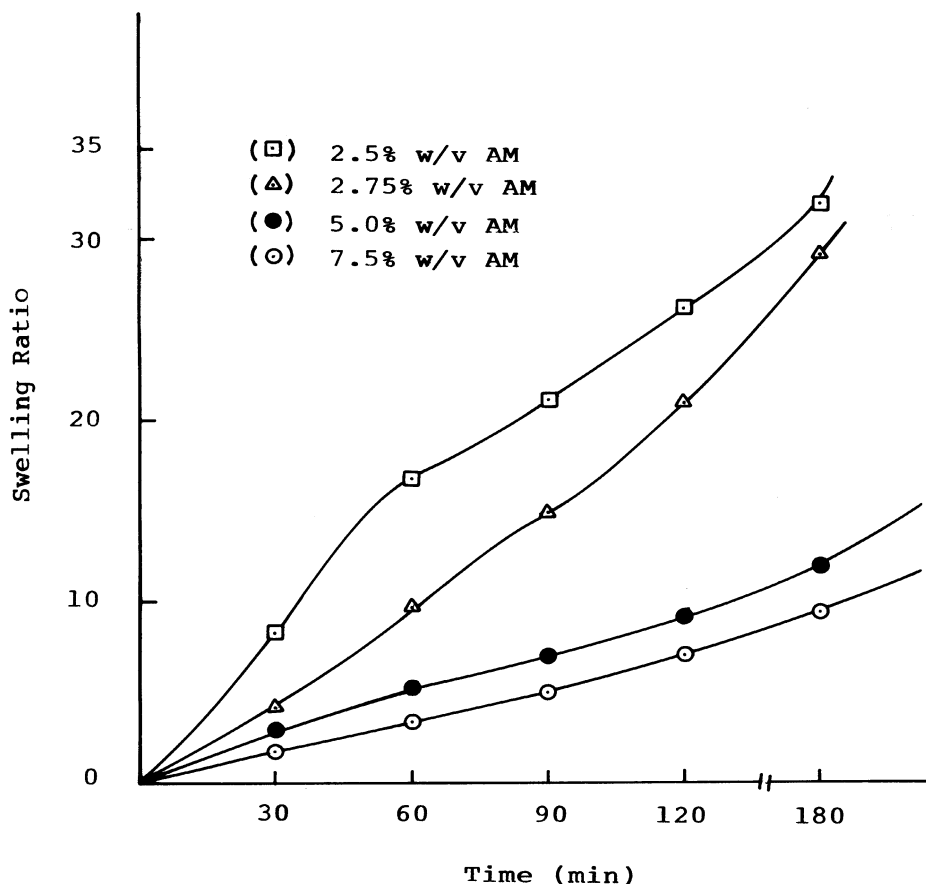


Figure 6. Variation in the swelling ratio of the IPN's with varying acrylamide (AM) content in the IPN's. [PEG] = 7.5% v/v, [CMC] = 2.0% w/v, [MBA] = 0.05% w/v, Temp. = 27°C.

volumes. This obviously results in a remarkable fall in the degree of swelling of the IPN.

Effect of pH

Macromolecular matrices containing either carboxyl groups or carboxylate ions as pendent functionals of network chains have been found to respond greatly to the external stimuli such as pH of the swelling medium. Such hydrogels or IPN's have been widely employed as pH-sensitive systems for targetted drug delivery [39]. In the present study, since the polymer used was the sodium salt of CMC, the network contained both COO^- and COOH groups along the CMC chains. To investigate the effect of pH on the swelling ratio of the IPN, the pH of the swelling medium was varied in the range 2.0 to 10.0 and the results are depicted in Fig. 8. The results clearly indicate that the

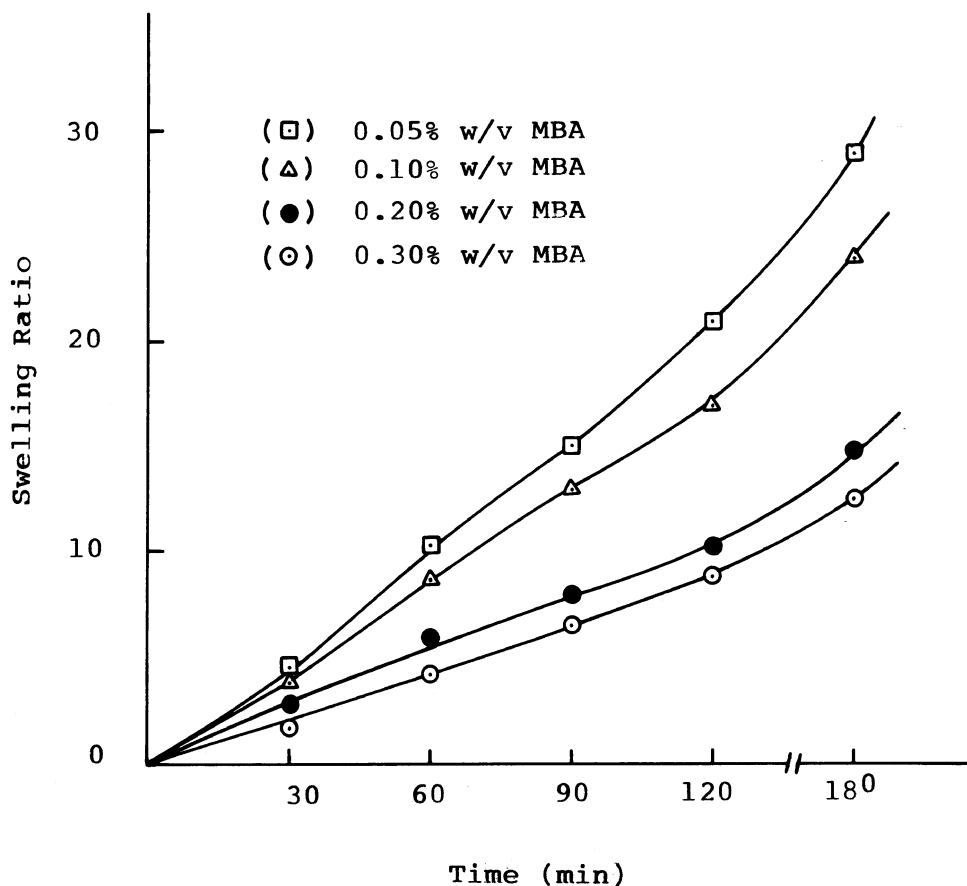


Figure 7. Effect of crosslinker (MBA) concentration on the swelling ratio of the IPN's. [PEG]=7.5% v/v, [CMC]=2.0% w/v, [AM]=3.75% w/v, [MBA]=0.05% w/v, Temp.=27°C.

degree of water sorption constantly increases with increasing pH of the medium. The observed increase in the swelling ratio can be explained by the fact that with rising pH of the swelling medium, the ratio COO^-/COOH on CMC also increases because of increasing ionization of carboxylic groups and this results in a greater repulsions among the COO^- bearing CMC chains. Thus, the existing repulsive forces causes CMC chains to undergo a faster relaxation which widens the mesh size of the free volumes and, subsequently allow greater number of penetrant water molecules to swell the IPN.

Another reason for the observed increase in the swelling ratio may be that with increasing pH, the amide groups ($-\text{CONH}_2$) of PAM chains undergo hydrolysis thus changing into $-\text{COOH}$ groups which also enhances the swelling.



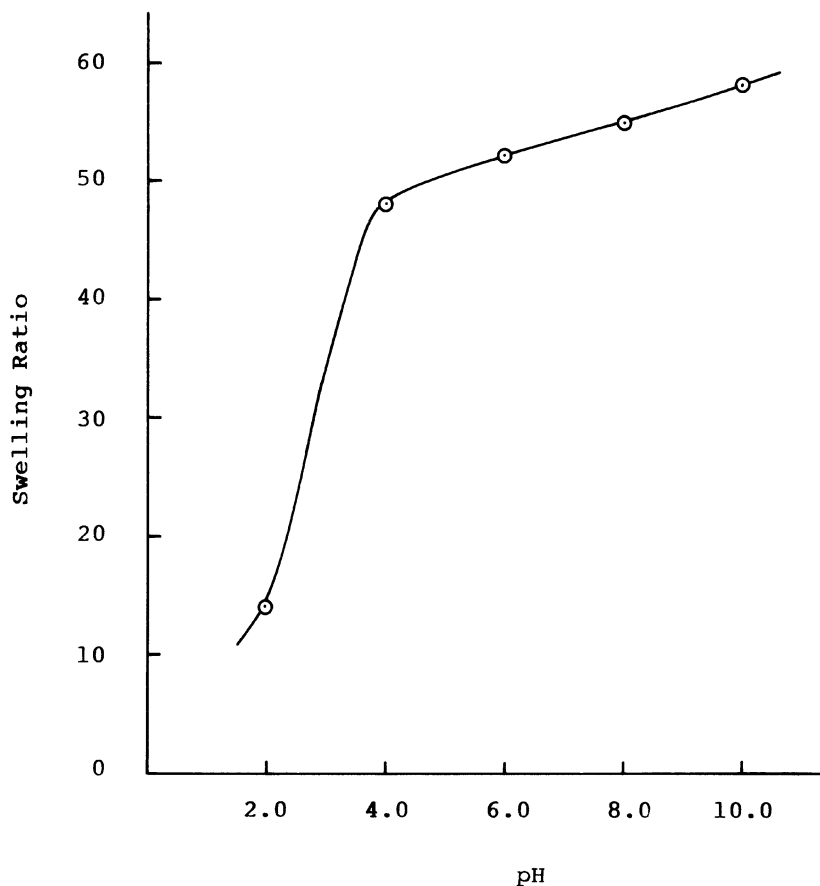


Figure 8. Effect of pH of the swelling medium on the swelling ratio of the IPN's. [CMC]=2.0% w/v, [PEG]=7.5% w/v, [AM]=3.75% w/v, [MBA]=6.05% w/v, Temp. = 27°C.

Effect of Temperature

The swelling behavior of a hydrogel is greatly concerned with temperature of the swelling medium as a rise in temperature affects the rate of diffusion of water molecules into the gel as well as that of relaxation of network chains. In addition a higher temperature may detach water molecules bound to the network chains and thus cause a fall in the degree of swelling. In the present study, the temperature of the swelling medium has been varied in the range 10 to 50°C and the results are depicted in Fig. 9. It is clear from the results obtained that whereas the swelling ratio of the IPN increases from 10 to 27°C a fall in the swelling ratio is noticed beyond 27°C. The results can be explained by the fact that in the initial range of increasing temperature both the diffusion of penetrant water molecules and relaxation



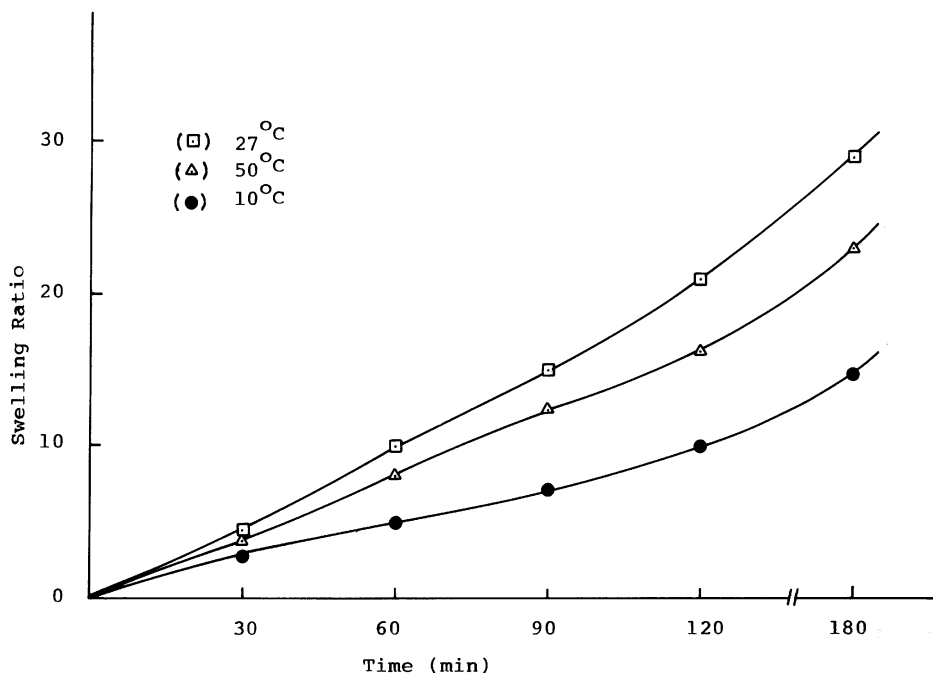


Figure 9. Effect of temperature on the swelling ratio of the IPN's. [PEG]=7.5% v/v, [CMC]=2.0% w/v, [AM]=3.75% w/v, [MBA]=6.05% w/v.

of network chains increase which result in an enhanced water-sorption of the IPN. However, beyond 27°C the fall observed in the swelling ratio may be attributed to the breaking of H-bonds between hydrogen of water and oxygen of PEG molecules of the specific hydrates formed during the swelling of the PEG network as reported elsewhere [40].

Effect of Salts

The swelling of a hydrogel results from a balance between the osmotic pressure of the swelling system and the elastic response of the network [36]. For a given network with definite elasticity, the swelling is mainly decided by the osmotic pressure of the gel which results from the difference between the mobile ion concentrations between the interior of the gel and external swelling medium. When the concentration of salt ions increases in the outer solution, the difference of mobile ion concentration between the polymer network and external solution decreases which, in turn, will reduce the swelling of the polymer gel.

The quantitative effect of salts on the swelling of the IPN can be best explained by the Donnan equilibrium theory which reveals that osmotic



pressure π_{ion} , responsible for swelling or deswelling of polymer network, is given by the following equation:

$$\pi_{\text{ion}} = \frac{(\Delta\mu^g - \Delta\mu^s)}{V_m} = 0 \quad (6)$$

where μ^g and μ^s are the chemical potentials of the solvent in the gel and solution respectively and V_m being the molar volume of the solvent.

Ignoring ion-ion, ion-solvent and ion-polymer interactions, one can write,

$$\pi_{\text{ion}} = RT \sum_i (C_i^g - C_i^s) \quad (7)$$

where C_i is the mobile ion concentration of species i . The above equation suggests that larger the difference between the ionic concentrations of gel and solution, greater would be the swelling.

Effect of Anions

In the present investigation the effect of electrolytes on the swelling of the IPN has studied by adding 0.05 M of chloride, carbonate and phosphate of sodium to the swelling medium. The results are depicted in Fig. 10 which imply that an appreciable fall in the swelling ratio of the IPN is noticed upon the addition of electrolytes. The observed decrease in the swelling ratio is obvious as the added salt ions cause a decrease in the term. The relative effectiveness of the added anions in depressing the swelling ratio obey the sequence given below,



The least effect of CO_3^{2-} ions may be due to the fact that Na_2CO_3 and Na_3CO_4 upon dissolution undergo salt hydrolysis and produce an alkaline solution which raises the pH of the swelling medium to alkaline range. On the other hand, sodium chloride gives a neutral solution upon dissolution. Since the swelling of the IPN increases with pH of the medium, the order of effectiveness of added anions is clearly explained.

Effect of Cations

The effect of cations on the swelling ratio of the IPN has been investigated by adding equimolar (0.05 M) amounts of chlorides of sodium, calcium and iron to the swelling medium. The results are depicted in Fig. 11,



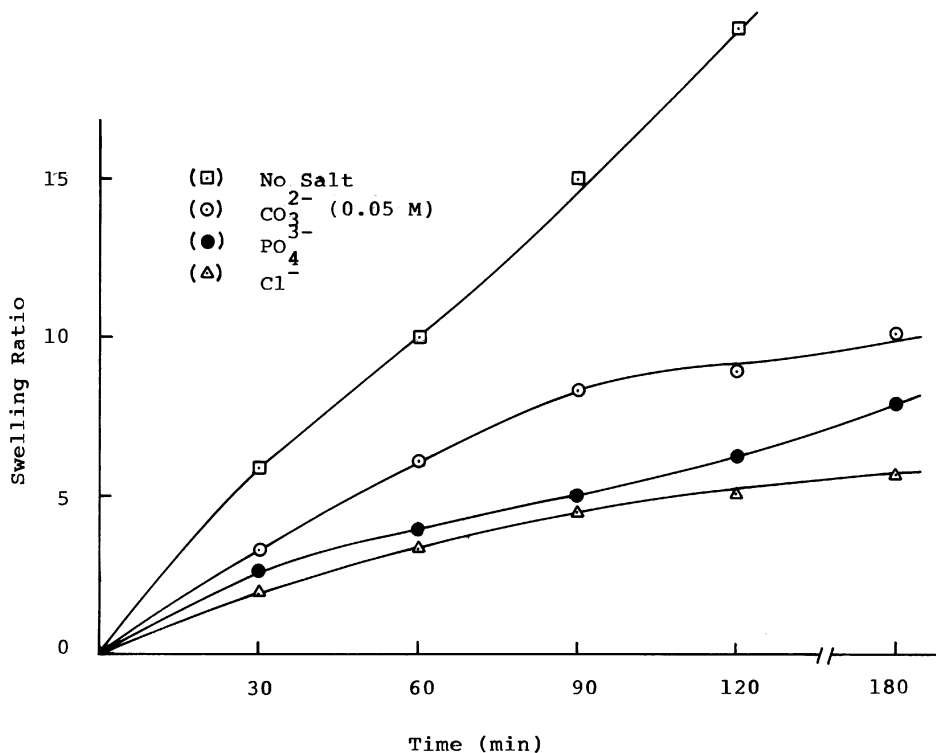


Figure 10. Effect of anions on the swelling ratio of the IPN's. [PEG]=7.5% v/v, [CMC]=2.0% w/v, [AM]=3.75% w/v, [MBA]=6.05% w/v, Temp.=27°C.

which indicate that the added cations substantially reduce the swelling ratio of the IPN. The observed fall in the swelling has already been explained previously. The order of effectiveness of the added cations follow the sequence as given below:



The sequence of the effectiveness can be attributed to the fact that ferric chloride upon hydrolysis produces an acidic solution and, therefore, suppress the swelling of the IPN due to protonation of carboxylate ion. On the other hand, dissolution of calcium and sodium chlorides results in an alkaline and neutral solutions respectively which do not cause much fall in the swelling ratio of the IPN's as caused by ferric chloride because of acidic pH. Thus, the effect of pH of the salt solution predominantly regulates the swelling behavior of the IPN's.

We also studied the effect of salt concentration of the swelling ratio of the IPN and noticed that a pronounced salt-effect could only be observed when the concentration of salts were ≥ 0.05 M. At lower concentration, i.e.,

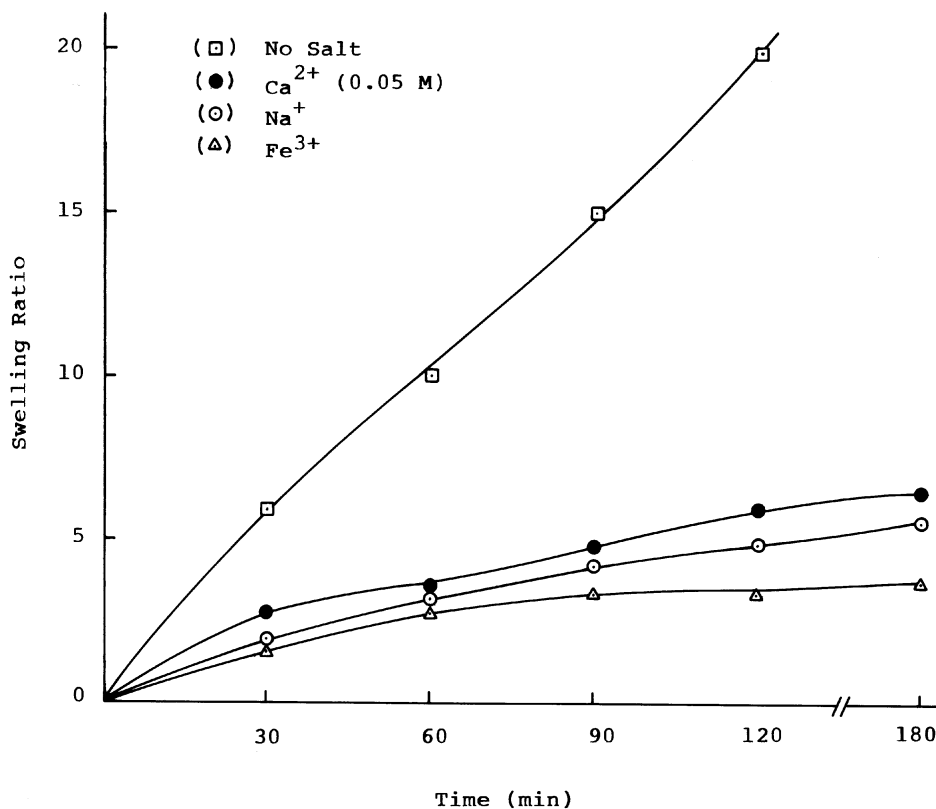


Figure 11. Effect of cations on the swelling ratio of the IPN's. [PEG]=7.5% v/v, [CMC]=2.0% w/v, [AM]=3.75% w/v, [MBA]=0.05% w/v, Temp.=27°C.

< 0.05 M all the salts displayed almost equal effects (results not shown). Similar type of results were also noticed by Lee et al. [41].

Analysis of Dynamic Sorption Data

Water transport mechanism in a swelling IPN is greatly contributed by numerous factors such as equilibrium water content, swelling rate, chemical composition of the hydrogel system, etc. In the present study, the dynamic water sorption experiments have been performed and the data have been analyzed in terms of swelling exponent 'n' and diffusion constants 'D' thus evolving a possible route of water transport. The following discussion correlates the plausible water transport mechanism and chemical architecture of the IPN. The whole data is summarized in Table 1.

When the concentration of CMC in the feed mixture of the IPN is increased from 0.5 to 2.0% w/v, the value of n is found to increase in the anomalous region and attains a value in the Super Case II region. The data



Table 1. Data Showing the Swelling Exponent (N) and Diffusion Constant (D) of Varying Compositions of the IPN's

Compositions (%)				n	DX10 ⁷ cm ² s ⁻¹	Mechanism
CMC w/v	PEG v/v	AM w/v	MBA w/v			
0.5	7.5	3.75	0.05	0.60	6.7	Anomalous
1.0	7.5	3.75	0.05	0.62	7.0	Anomalous
1.5	7.5	3.75	0.05	0.87	4.3	Anomalous
2.0	7.5	3.75	0.05	1.33	6.7	Super Case II
2.0	5.0	3.75	0.05	0.8	2.7	Anomalous
2.0	7.5	3.75	0.05	0.93	8.1	Anomalous
2.0	10.0	3.75	0.05	1.10	10.2	Super Case II
2.0	7.5	3.75	0.05	1.42	6.7	Super Case II
2.0	7.5	5.0	0.05	0.85	2.7	Anomalous
2.0	7.5	10.0	0.05	0.75	4.3	Anomalous
2.0	7.5	3.75	0.1	0.85	5.4	Anomalous
2.0	7.5	3.75	0.2	0.90	4.5	Anomalous
2.0	7.5	3.75	0.3	0.98	2.7	Case II

reveal that with increasing CMC, the swelling process shifts from less relaxation controlled to more relaxation controlled (anomalous range) and ultimately acquires a super case II value. The observed findings can be explained by the fact that with increasing CMC content in the IPN, the network density will increase and this will result in a lower relaxation rate of macromolecular chains of the IPN. At much greater content of the CMC the observed super case II may be due to large hydrophilic nature of the IPN.

In the case of variation in the PEG content of the IPN in the range 5.0 to 10.0% v/v, the swelling exponent is found to increase from an anomalous range to a super case II value as noticed with CMC also. This clearly implies that with increasing the content of hydrophilic PEG, the swelling process becomes increasingly relaxation controlled and finally attains a super case II value due to increased hydrophilicity of the IPN.

A reverse trend is observed when the concentration of AM increases in the feed mixture in the range 3.75 to 10.0% w/v. The corresponding n values summarized in Table 1 suggest that there occurs a decrease in the swelling exponent n from Super Case II value to anomalous region. This implies that an increased number of PAM chains in the IPN shifts the swelling process to decreasing relaxation controlled nature. The results can be explained by the fact that with increasing AM the molecular weight of PAM chains increases which facilitate the relaxation of PAM chains and thus causing the swelling process to become less and less relaxation controlled.

Another important parameter that also affects not only the equilibrium swelling ratio of the IPN but also the mechanism of water transport is the



crosslinked density of the network. In the present work, an increasing crosslinked density of the IPN has been achieved by increasing the crosslinker (MBA) content in the feed mixture in the range 0.1 to 0.3% w/v. The numerical value of n summarized in Table 1 indicate that the value of n is increasing in the anomalous region thus implying for an increasing relaxational controlled swelling process. The results can be attributed to the fact that with increasing crosslinked density of the IPN, the macromolecular network becomes more compact and this results in an increasing restriction in the free relaxation of network chains. Thus, the swelling process tends to acquire relaxation controlled nature.

Release of KNO_3

The release of an active agent from swellable polymeric matrix is based on the glassy-rubbery transition of the polymer which occurs as a result of water penetration into the matrix [42]. Whereas interactions between water, polymer and active agent are the primary factors in release control, various formulation variables also influence the release rate to a greater or lesser degree. Thus, the extent of the loaded compound [43], active agent (or drug): polymer ratio [44], drug-particle size [45], etc. have been identified as modifiers of the release kinetics. Other important factors which govern the time course of the release process are the dissolution of the diffusate, surface area of the diffusate particles and molecular size and permeability of the diffusate molecules through the network.

The release kinetics of a loaded IPN is closely related to its water sorption kinetics [46] as it has already been established that a highly swelling network should release a greater amount of active solute entrapped within the network. The release of solute from loaded network (initially dried) involves the absorption of water into the matrix and simultaneous release of solute via diffusion, as governed by Fick's law. The process can be modelled using a free volume approach or a swelling controlled release mechanism.

Now, we discuss our results on the release of KNO_3 from loaded IPN's under varying experimental conditions.

Effect of Loading

An important aspect in the use of hydrogels as the carrier of active compounds is the effect of percent loading on the rate of solute release. For this purpose, the IPN's were equilibrated with KNO_3 solutions of varying concentrations for three days. The loaded IPN's were placed in release medium and the progress of the release process was monitored conductometrically. The release profiles are depicted in Fig. 12 which indicate



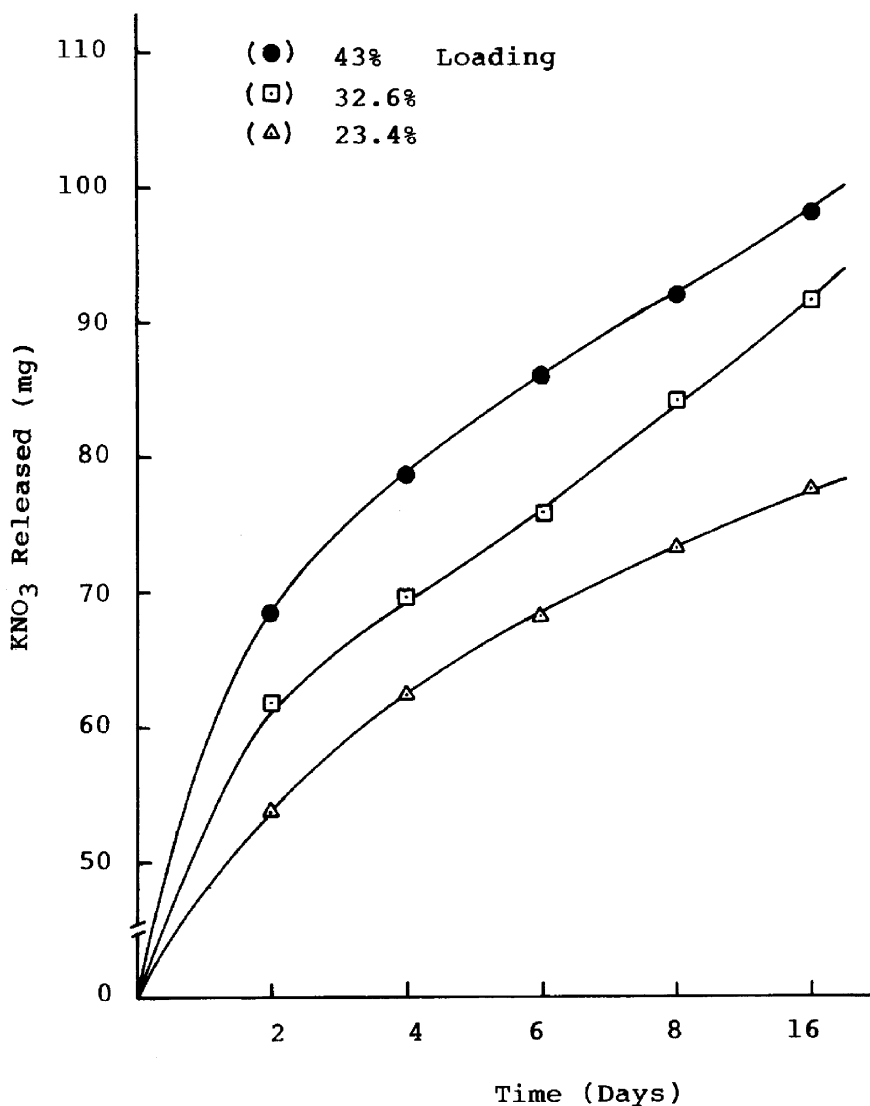


Figure 12. Effect of %loading of KNO_3 on the release profiles of the IPN's. [PEG]=7.5% v/v, [CMC]=2.0% w/v, [AM]=3.75% w/v, [MBA]=6.05% w/v, Temp.=27°C.

that the amounts of released KNO_3 increase with increasing percent loading of the IPN. The results are quite expected as larger the initial load, the faster is the movement of the solvent front penetrating the surface of the loaded IPN [47]. A larger loading of the IPN may also facilitate the relaxation of macromolecular chains.

Effect of CMC

The effect of CMC content of the IPN has been investigated on the release profiles of KNO_3 by employing 1.0 to 2.0% w/v of the CMC into the feed mixture of the IPN's and then equilibrating them with 1.0% solution of KNO_3 for 72 hours. The loaded IPN's were dried and thus the device was obtained. The progress of the release process was monitored conductometrically. The results are displayed in Fig. 13 which indicate that the release rate as well as the amounts of released KNO_3 increase with increasing CMC content in the IPN.

The observed results can be explained by the fact that with increasing CMC in the IPN's the hydrophilicity of the network also increases and this consequently results in penetration of greater number of water molecules into the gel matrix causing relaxation of macromolecular chains. This obviously results in a faster diffusion of entrapped KNO_3 from within the IPN to the exterior release medium following either Fickian or non-Fickian release. The release findings, therefore, are in good consistency with our swelling experiment results.

Effect of PEG

As PEG is another hydrophilic polymer and a constituent of the IPN in the present study, its effect on the release kinetics of KNO_3 has been studied by varying PEG in the range 2.5 to 7.5% v/v in the feed mixtures of the IPN's. The results on the release study are shown in Fig. 14, which reveal that the both the release rate and released amounts increase with increasing PEG content in the IPN's. The observed results are quite obvious and can be attributed to the fact that increasing PEG results in a larger swelling of the networks and, therefore, will also give rise to a faster release rate of KNO_3 . It has also been well recognized that the transport of water-soluble conditions can be many powers of ten faster in a hydrated hydrogel than in a hydrophobic polymer. In fact a water-swollen hydrogel is a two component system which may be imagined as a physically strong polymer network structure between the strands of which are water-filled permeation channels. Thus, a hydrated network always favors enhanced release.

Effect of AM

The influence of the polymerizable hydrophilic monomer acrylamide on the release profiles of KNO_3 has been investigated by charging the feed mixture of the IPN's with increasing amounts of AM in the range 5.0 to 10.0% w/v. The synthesized IPN's were loaded with KNO_3 and subsequent release results are shown in Fig. 15. The results indicate that both the release



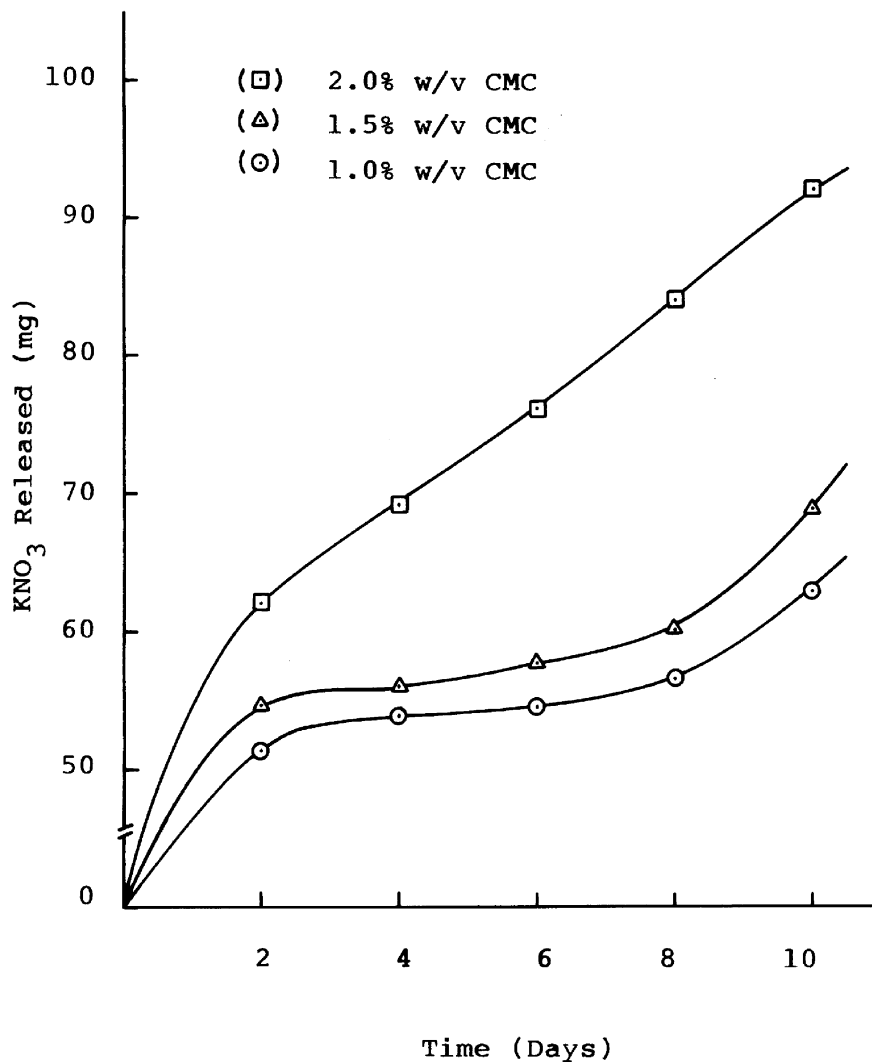


Figure 13. Effect of CMC content of the IPN's on the release rate of KNO_3 . [PEG] = 7.5% v/v, [AM] = 3.75% w/v, [MBA] = 0.05% w/v, Temp. = 27°C.

rate and released amounts increase with increasing AM content in the IPN's. The observed findings are not consistent with our swelling results as we noticed a fall in the swelling ratio with increasing AM content in the swelling network. However, the results can be explained by the fact that increasing AM content in the IPN may cause a greater degree of interactions with the loaded KNO_3 and, thus, may facilitate the process of relaxatin of



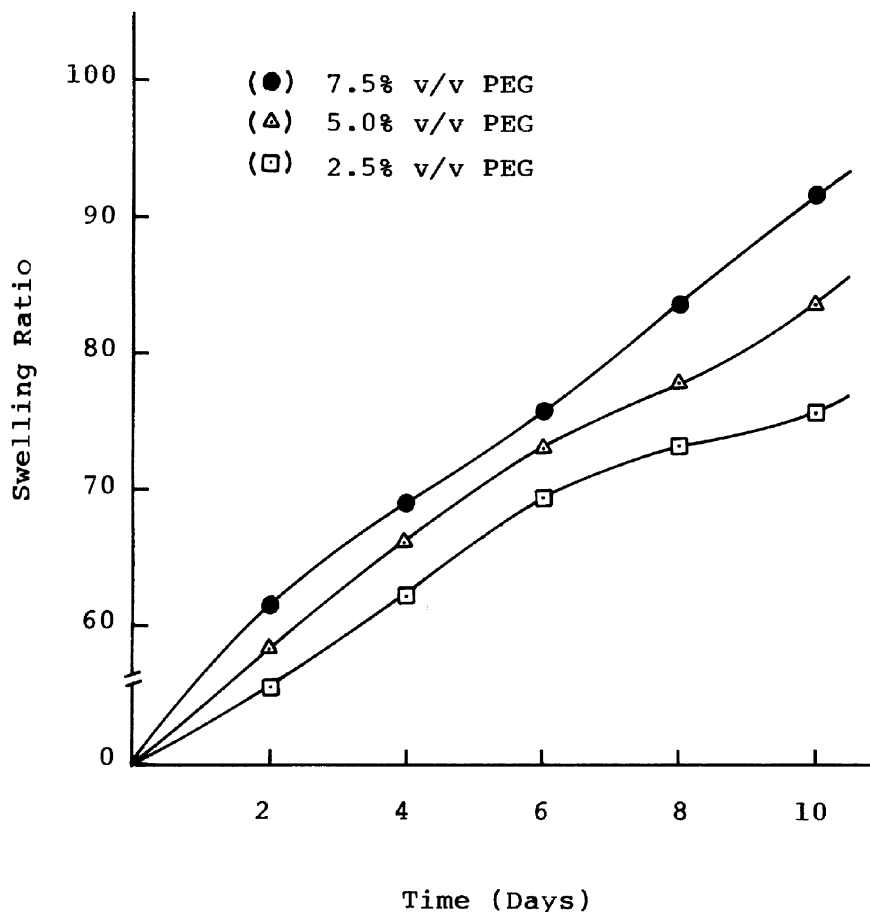


Figure 14. Effect of PEG content of the IPN's on the release rate of KNO_3 . $[\text{CMC}] = 2.0\%$ w/v, $[\text{AM}] = 3.75\%$ w/v, $[\text{MBA}] = 0.05\%$ w/v, Temp. = 27°C .

macromolecular chains of the IPN network. This will certainly lead to a higher release rate and released amount of KNO_3 .

Effect of Crosslinker

When the amount of crosslinker (MBA) increases in the feed mixture of the IPN in the range 0.05 to 0.3% w/v the resulting IPN's possess more compact and crosslinked networks which show a decreasing degree of swelling. Similar type of results have also been observed in release study of these IPN's. The results are shown in Fig. 16 which reveal that both the release-rate and amounts of released KNO_3 decrease with increase in MBA content of the IPN's.



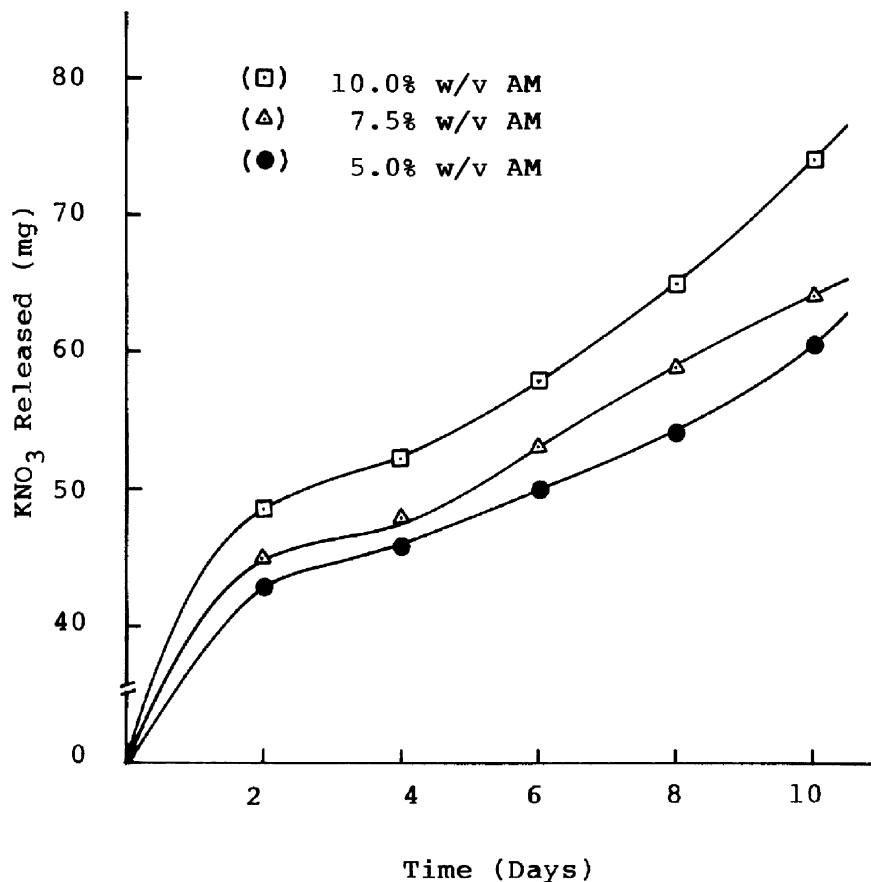


Figure 15. Effect of AM content of the IPN's on the released amounts of KNO_3 . [PEG]=7.5% v/v, [CMC]=2.0% w/v, [MBA]=0.05% w/v, Temp. = 27°C.

The results can be attributed to the fact that a largely crosslinked IPN produces a matrix with small mesh sized free volumes and, therefore, accommodate less amounts of KNO_3 . This clearly explains lower release-rate and lower released amounts of KNO_3 . Another cause may be that because of small mesh sizes of the free volumes the diffusion of water molecules into the gel-matrix and that of KNO_3 from within the matrix become relatively slower and this as a consequence, favours lower release rate of KNO_3 . A fall in the release rate and released amounts of KNO_3 may also be due to a poor relaxation rate of macromolecular chains of the loaded IPN's which will obviously result in a slow release kinetics.



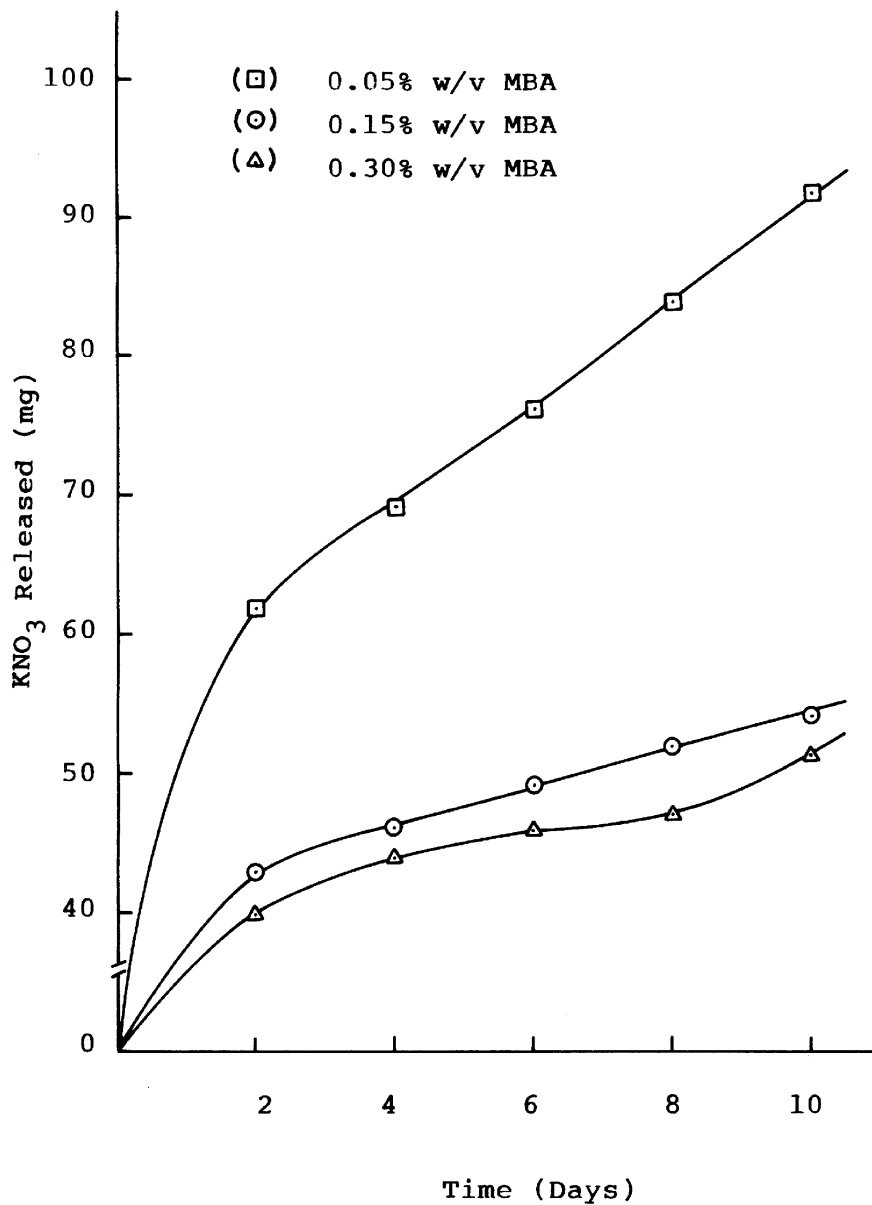


Figure 16. Effect of crosslinker (MBA) content of the IPN's on the release rate of KNO_3 . [PEG] = 7.5% v/v, [CMC] = 2.0% w/v, [AM] = 3.75% w/v, Temp. = 27°C.

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CONCLUSION

Incorporation of crosslinked polyacrylamide (PAM) chains into a hydrophilic network of carboxymethyl cellulose (CMC) and polyethylene glycol (PEG) results in a ternary interpenetrating polymer network (IPN) with large water sorption capacity. The IPN exhibits an increasing swelling tendency when the PEG and CMC contents are increased in the range 9.5 to 10.0% v/v and 0.5 to 2.0% w/v, respectively. On the other hand, a decrease in the swelling ratio of the IPN is noticed when the monomer acrylamide (AM) and crosslinker (MBA) content increase in the feed mixture of the IPN in the range 3.75 to 10% w/v and 0.05 to 0.30% w/v, respectively. In addition to the chemical architecture of the network the swelling is also influenced by the pH and temperature of the swelling medium. In the case of pH the swelling is found to increase with increasing pH of the external medium in the studied range of 2.0 to 10.0. A rise in temperature also results in an increase in the swelling ratio while a fall is observed in the higher temperature range. The presence of salt ions in the release medium exert a negative influence on the swelling capacity of the IPN.

The chemical composition of the IPN also influences the mechanism of water transport. With increasing CMC content in the IPN the swelling mechanism shifts from anomalous to Super Case II. A similar variation in sorption mechanism is observed with decreasing AM and increasing PEG content in the IPN's. On the other hand, increasing crosslinked density of the IPN results in a shift of water transport from anomalous to case II value.

The IPN's also display potential for acting as a carrier of agrochemicals (such as KNO_3). It is found that the loaded IPN's continuously release KNO_3 up to 10 days. The release rate and amount of released KNO_3 increase with increasing CMC, PEG and AM while the increasing crosslinker content slows down both the release rate and released amounts of KNO_3 .

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