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Swelling and dye adsorption properties of radiation induced *N*-vinyl-2-*pyrrolidone*/acrylonitrile hydrogels

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Summary

Swollen hydrogels were prepared by γ-radiation copolymerization of N-vinyl-2-pyrrolidone and acrylonitrile. The influence of radiation dose and feed composition on the swelling properties, diffusional behavior of water and diffusion coefficients of the hydrogel systems were examined. N-vinyl-2-pyrrolidone/acrylonitrile hydrogels were swollen in the range 50-850%. Water diffusion to the hydrogels generally was a *non-Fickian* type diffusion.

The hydrogel were used in the studies of adsorption of some water soluble dye such as basic blue 9, tetraethyl rhodamine, xylidine ponceau 2R, indigo carmine, helianthin and erythrosine, and of a vitamin riboflavin (Vitamin B_2).

Introduction

Hydrogels are crosslinked hydrophilic polymers that are swollen in water usually to equilibrium. If the water content is increased up to very high values, the decline in mechanical properties is unacceptable for most purposes. Many authors emphasised the ways improved mechanical properties can be achieved by control of chemical (covalent) and physical (especially hydrophobic) crosslinking. It was pointed out that small cluster of hydrophobic groups in a predominantly hydrophilic network may serve to increase load bearing yet with avoidance of the embrittlement caused by carbon-carbon crosslinks[1]. Hydrophobic groups have been introduced by copolymerization of various hydrophobic monomers with hydrophilic monomers such as acrylamide, 2-vinyl-N-pyrrolidone, and 2-hydroxyethylmethacrylate (1-4).

Hydrogels have been used and applied in bioengineering, biomedicine, pharmaceutical, veterinary, food industry, agriculture, photographic technology and other fields. They are used as controlled release systems of drugs, for production of contact lenses and artificial organs in biomedicine, as adsorbents for removal of some agents in environmental applications, in immobilized enzyme kinetics in bioengineering and also as carriers of water, pesticides and fertilizer in agriculture (5-11). Highly swollen hydrogels have been reported to be based on poly(N-vinyl-2-pyrrolidone) networks prepared by polymerization of N-vinyl-2-pyrrolidone (VP) and crosslinking agents through radiation crosslinking of aqueous solutions of VP by one of the our collaborators (12,13).

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In the present paper, N-vinyl-2-pyrrolidone/acrylonitrile (VP/AN) hydrogels were prepared from VP (a hydrophilic monomer) with a hydrophobic monomer such as acrylonitrile (AN) by irradiating γ-rays at various doses. Swelling properties and diffusional parameters of the hydrogels were investigated. The hydrogel was used in adsorption of some water soluble dyes such as basic blue 9, tetraethyl rhodamine, xylidine ponceau 2R, indigo carmine, helianthin and erythrosine, and of a vitamin riboflavin (Vitamin B_2).

Experimental

For the preparation of hydrogels; 1, 2, 3 or 4 ml of N-vinyl-2-pyrrolidone (d=1080 kg m^{-3}) (VP) (Fluka AG, Buchs, Switzerland) was mixed with 1 ml of acrylonitrile (d=806 kg m^{-3}) (AN) (BDH, Poole-UK). These solutions were placed in PVC straws of 3 mm in diameter and irradiated at 14.75, 17.70, 20.65 and 26.55 kGy in air at ambient temperature in a ^{60}Co Gammacell 220 type γ irradiator at a fixed dose rate of 0.58 kGy hr^{-1}. The dose rate was determined by the conventional Fricke dosimeter. Fresh N-vinyl-2-pyrrolidone/acrylonitrile (VP/AN) hydrogels obtained in long cylindrical shapes were cut into pieces of 5-7 mm in length. They were dried in air and a vacuum, and stored for swelling studies.

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

About 1 g VP/AN (4VP:1AN and irradiated to 14.7 kGy) hydrogels were transferred into 100 mL of solutions of each dyes, and allowed to equilibrate for five days at 25 °C. These aqueous solutions were separated from the hydrogels by decantation. Spectrophotometric measurements carried out using a Philips PO 8715 model spectrophotometer at ambient temperature. The absorbances of these solutions at desired wavelengths. Distilled water was used as a reference. The equilibrium concentrations of dyes were measured by means of precalibrated scales.

Results and Discussion

Ionizing radiation is very useful in producing polymers from monomeric units and in modifying the properties of preexisting polymers. Ionizing radiation provides a very clean method for the obtention and modification of polymers. No chemicals or catalysts have to be added to the reaction matrix. The polymerization achieved by free radicals (occasionally ions) created in the material at the end of process. Therefore, no chemicals or catalysts remain in the material by radiation (14).

The radiation technique seems to be promising for preparation of hydrogels because a polymer in aqueous solution or water-swollen state readily undergoes crosslinking on irradiation to yield a gel-like material. Since the hydrogel is not contaminated with foreign additives and crosslink is formed by stable C-C bonds, it is of interest to study the preparation of hydrogels by irradiation(15,16).

For preparation VP/AN copolymers along with ionizing radiation processing were used in this study. When monomers of VP and AN are irradiated with ionization rays such as γ-rays,

one of double bonds of -C=C- on the monomers breaks with the effect of ionization irradiation and free radicals are generated. Then these free radicals react with each other, and a copolymer of VP/AN is formed.

When irradiation dose is increased during ionising radiation of VP and AN, the polymer chains crosslink and then gels are obtain. Gelation of VP/AN copolymers occurs at a dose 14 kGy of γ ray irradiation doses at ambient temperature (17). So, a dose of 14.75 kGy of γ rays is the base for preparation of VP/AN hydrogels. Dried gels are of glassy form and very hard, but swollen gels are soft. The hydrogels are obtained in the form of cylinders. Upon swelling, the hydrogels retained their shapes.

In this study, after some experiment observations and results, it is seen that the suitable conditions for preparation of the hydrogels are 14.75-26.55 kGy of γ-rays doses and the binary mixtures of VP: AN 1: 1-1:4 by volume in ml. On the other hand, commercial PVP and AN monomer are irradiated with together, but no gelation is shown at the end of irradiation. It can be said that, copolymerization of VP with AN is takes place, during ionizing radiation and there is not any graft copolymerization of AN on the crosslinked copolymeric system.

A fundamental relationship exists between the swelling of a polymer in a solvent and the nature of the polymer and the solvent. Swelling is one of the most important parameters about swelling studies. The swelling (%S(m)) was calculated from the following relation (8,9,18):

$$\%S(m) = ((m_t - m_o)/m_o) \times 100 \qquad 1$$

where m_t is the mass of the swollen gel at time t and m_o 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 VP/AN copolymers were plotted and representative swelling curves are shown in Figure 1. If Figure 1 is examined, it can be seen swelling is increased by time, however, awhile this becomes a constant swelling. This value of swelling may be named equilibrium of mass swelling. The values of equilibrium swelling of VP/AN copolymers are used for the calculation of some network characterization parameters, and given Table 1.

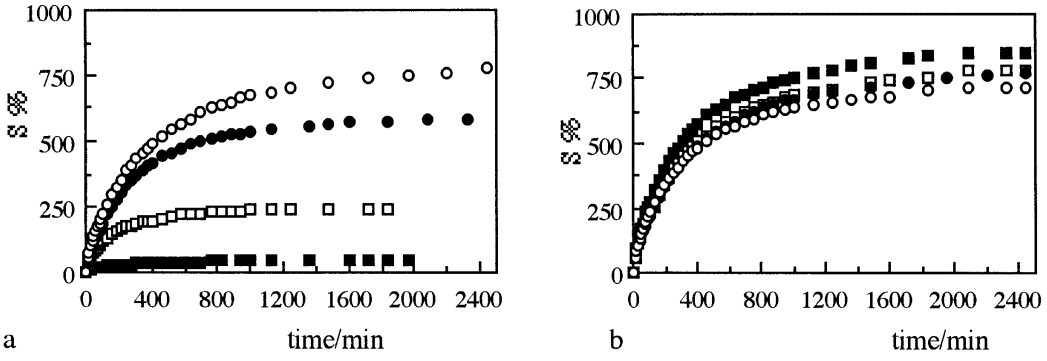

Figure 1. The swelling curves of VP/AN hydrogels.
a. Total dose given 20.65 kGy. (■); 1VP:1AN, (□); 2VP:1AN, (●); 3VP:1AN, (o); 4VP:1AN.
b. The ratio of 4 VP:1 AN. (■); 14.75 kGy, (□); 17.70 kGy, (●); 20.65 kGy, (o); 26.55 kGy.

Table 1. The values of equilibrium swelling and swelling rate constant of VP/AN hydrogels.

Dose	14.75 kGy		17.70 kGy		20.65 kGy		26.55 kGy	
VP:AN	S_{eq} %	$k_{0.5} x10^2$	S_{eq} %	$k_{0.5} x10^2$	S_{eq} %	$k_{0.5} x10^2$	S_{eq} %	$k_{0.5} x10^2$
1:1	45	0.017	45	0.018	50	0.021	50	0.018
2:1	240	0.125	240	0.120	240	0.120	270	0.117
3:1	645	0.230	625	0.223	585	0.227	495	0.167
4:1	850	0.312	780	0.288	775	0.260	715	0.261

Table 1 shows that the values of equilibrium swelling of the gels are among 50-850 %. On the other hand, the equilibrium swelling of VP/AN hydrogels in the ratios of 4VP:1AN and 3VP:1AN are decreased with the increase of the irradiation dose, whereas the equilibrium swelling of VP/AN hydrogels in the ratios of 2VP:1AN and 1VP:1AN are constant with the increase of the irradiation dose. If the content of VP in the hydrogels is increased, the equilibrium swelling of the hydrogels is increased. The reason of these is the hydrophilic group on the VP. If irradiation dose is increased, the number of the small chains is increased at unit copolymerization time and the crosslink density of VP/AN copolymeric system is higher than the lower irradiation doses. At the same time, the number-average molar mass of the between crosslinks is smaller than at the lower γ ray doses. For understanding of variation of swelling of the hydrogels with the VP content and irradiation dose, the graphs of the values of the equilibrium swelling of the hydrogels versus the contents of VP, and versus irradiation doses are plotted and shown in Figure 2.

To determine of swelling rate coefficient, degree of swelling for the VP/AN hydrogels vs. the square root of immersion time were plotted, and representative curves are shown in Figure 3a. Swelling rate coefficients were calculated from the slopes of the straight portion of the curves (27) in Figure 3a, and are shown in Table 1. Table 1 shows that the swelling rate coefficients of VP/AN hydrogels decreased with the increase of the irradiation dose, whereas these

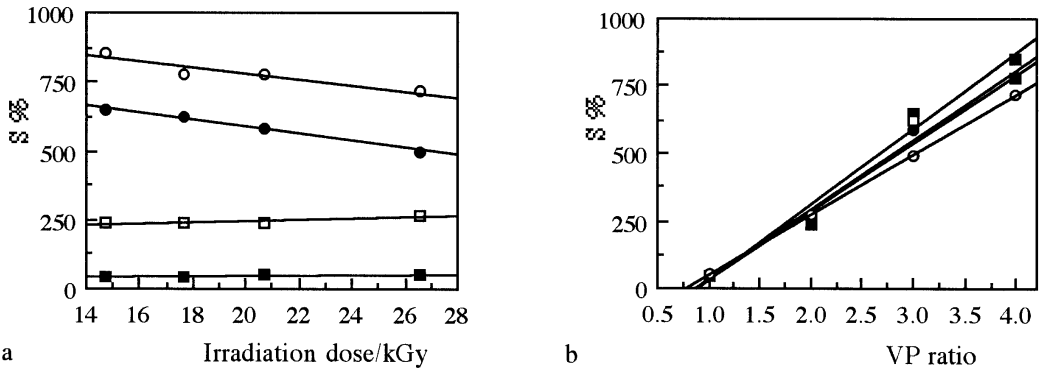

Figure 2. Effect of irradiation dose (a), and VP ratio (b) on the swelling of VP/AN hydrogels.
a. (■); 14.75 kGy, (□); 17.70 kGy, (●); 20.65 kGy, (o); 26.55 kGy.
b. (■); 1VP:1AN, (□); 2VP:1AN, (●); 3VP:1AN, (o); 4VP:1AN.

parameters increased with the increase the content of VP in VP/AN copolymers. Furthermore, It can be said that the hydrogels swells faster with increase of VP content than with increase of irradiation dose.

Analysis of the mechanisms of water diffusion in swellable polymeric systems has received considerable attention in recent years because of the important applications of swellable polymers in the biomedical, pharmaceutical, environmental, and agricultural fields (18). The following equation was used to determine the nature of diffusion of water into hydrogels

$$F = k\, t^{n} \qquad 2$$

where F denote the fraction of solvent which diffused into the gel at time t, 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 non-Fickian type. This equation is applied to the initial stages of swelling and plots of ln F versus ln t yields straight lines up to almost a %60 increase in the mass of hydrogel (8,9,18). For the hydrogels, ln F versus ln t plots were drawn using the kinetics of swelling and some representative results are shown in Figure 3b.

The n and k were calculated from the slopes and intercepts of the lines, respectively. The values of diffusion constants and diffusional exponents of VP/AN copolymers are listed in Table 3. In Table 3, it is shown that the values of diffusional exponent are ranged between 0.45 and 0.67. In the experiments, the number to determine type of diffusion (n) was found to be over 0.50 except three copolymers in the ratio of 1AN:1VP. Hence the diffusion of water into VP/AN copolymers were taken as a *non-Fickian* character (18). This is generally explained as a consequence of slow relaxation of polymer matrix.

The volume swelling parameters were used to calculate the diffusion coefficient and the intrinsic diffusion coefficient. 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 (20).

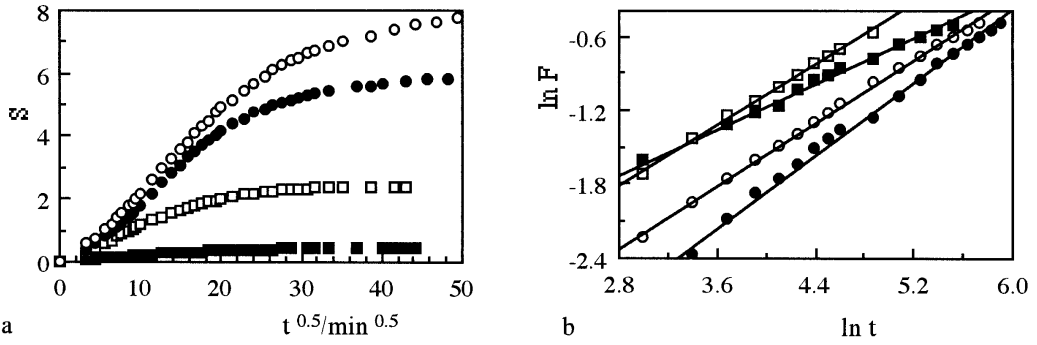

Figure 3 a. Effect of VP ratio on the time course of swelling of VP/AN copolymers (total dose 20.65 kGy); b. The plots of ln F versus ln t for VP/AN copolymers (total dose: 14.75 kGy). (■); 1VP:1AN, (□); 2VP:1AN, (●); 3VP:1AN, (o); 4VP:1AN.

Table 2. The values of n , k ($x10^2$), and the diffusion and the intrinsic diffusion coefficient ($x10^6$ cm^2 s^{-1}) for VP:AN copolymers.

Dose	14.75 kGy				17.70 kGy				20.65 kGy				26.55 kGy			
VP:AN	k	n	D	$\mathcal{D}$	k	n	D	$\mathcal{D}$	k	n	D	$\mathcal{D}$	k	n	D	$\mathcal{D}$
1:1	4.78	0.47	1.16	1.21	5.61	0.45	1.42	1.47	4.28	0.51	1.42	1.49	5.42	0.44	1.12	1.18
2:1	2.99	0.61	2.01	2.47	3.12	0.60	1.95	2.40	3.42	0.57	1.91	2.38	4.27	0.51	1.57	2.03
3:1	1.34	0.66	1.02	1.86	1.31	0.67	1.04	2.04	1.39	0.67	1.22	2.24	2.46	0.55	1.05	1.77
4:1	1.64	0.64	1.29	2.14	1.83	0.62	1.30	2.02	1.73	0.61	1.06	2.21	1.97	0.60	1.29	2.03

In hydrogel characterization, diffusion coefficient was calculated from the following relations:

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

where D is expressed cm^2 s^{-1}; t is the time at which the swelling is one half the equilibrium value (V/V_o=1/2) and 1 is the radius of cylindrical polymer sample. The intrinsic diffusion coefficient may be expressed as

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

where V is volume fraction of solvent penetrating the polymer by time t, defined above (20).

Table 2 shows that the values of the intrinsic diffusion coefficient of VP/AN hydrogels are greater than their values of the diffusion coefficient, because equation 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 case where no mass action effects enter (20).

To observe adsorption of some dyes, VP/AN hydrogel in the ratio of 4 VP:1 AN and irradiated 14.75 kGy were selected, because the hydrogel were showed a maximum swelling in the VP/AN system.

In order to determine the partition coefficient for the VP/AN hydrogel, gel was placed in aqueous solutions of cationic dyes such as basic blue 9 and tetraethyl rhodamine, and the aqueous solutions of anionic dyes such as xylidine ponceau 2R, indigo carmine, helianthin and erythrosine, and a vitamin such as riboflavin (Vitamin B_2), and allowed to equilibrate for five days. At the end of this time, VP/AN hydrogels in the solutions of dyes showed the dark colorations of the colors of the original solutions. The concentration of surrounding solution was monitored using UV-VIS spectroscopy.

The mass of adsorbate per unit mass of adsorbent, q_e can be calculated from the following relation,

$$q_e = \frac{C_i - C}{m} x V_t \qquad 5$$

Where q_e is in mg adsorbate per gram g dry adsorbent, C_i and C are the initial and equilibrium concentrations of solution of adsorbate in mg L^{-1}, V_t is volume of solution of adsorbate in L and m is mass of dry adsorbent in g.

Table 4. Some sorption properties of VP/AN copolymers.

Name	$C_{initial}$ / mg L^{-1}	q_e / mg g^{-1}	K_d
Basic blue 9	25	0.43	0.205
Tetraethylrhodamine	25	0.36	0.315
Riboflavin (Vitamin B_2)	50	3.35	0.720
Xylidine ponceau 2R	50	2.20	0.786
Indigocarmine	50	2.30	0.852
Helianthin	40	1.88	0.887
Erythrosine	25	1.85	2.846

The partition coefficient of the a solute between in solution and on adsorbent, K_d, was calculated as,

$$K_d = C_m / C_s \qquad 6$$

Here C_m is the concentration of the solute in the hydrogel, C_s is the concentration in the solution after equilibrium has been reached. The concentrations are in mg L^{-1}. The masses of adsorbed dyes gram of dry hydrogel (q_e) and partition coefficients of the dyes (K_d) between solution and hydrogels were calculated, and are shown in Table 3.

In Table 3, it is shown that the values of partition ratio of basic blue 9 and tetraethyl-rhodamine are small than the values of partition ratio of xylidine ponceau 2R, indigo carmine, helianthin and riboflavin (Vitamin B_2), whereas this value of erythrosine is very high. Basic blue 9 and tetraethylrhodamine are cationic dyes while other dyes are anionic in character. On the other hand, erythrosine is either anionic in character or containing iodide.

PVP can be cationic in character on the polar lactam ring because of the resulting of keto-enol tautomerism (21). Furthermore, hydrophobic interactions and hydrogen bonding (22-24) can be occur between VP and cationic dyes while cationic repulsions can be occurs between cationic groups of VP and basic blue 9 and tetraethylrhodamine. Whereas, electrostatic interactions with together hydrophobic interactions and hydrogen bonding can be occur between cationic groups of VP and anionic groups of the other dyes. On the other hand, it is reported that PVP shows the high affinity to iodide (25). So, VP/AN hydrogel was sorbed erythrosine more than other dyes. The differences in the values of partition ratio can be resulting of these evaluations. On the other hand, only, the value of the partition ratio of erythrosine is higher than 1. So, it can be said that VP/AN hydrogel is good absorbent for erythrosine, but it is poor absorbent for the other anionic dyes used in this study, while it is not an adsorbent for cationic dyes.

Conclusion

For VP/AN copolymers, it is found that favourable VP contents are in the range of 1-4 ml of VP with 1 ml of AN and favourable irradiation doses are in the range of 14.75-26.55 kGy. VP/AN copolymers swelled among 50-850%, Water diffusion to VP/AN hydrogels generally was of *non-Fickian type* diffusion. Evaluations of volume swelling studies shows that the

diffusion and the intrinsic diffusion coefficient increased by increasing quantities of VP. The number-average molar mass between crosslinks increased by increasing quantities of VP in the hydrogels and decreased by increasing irradiation doses, while crosslink density and numbers of elastically effective chains decreased by increasing quantities of VP in the hydrogels and increased by increasing irradiation doses. Basic blue 9, rhodamine B, xylidine ponceau 2R, indigo carmine, helianthin and erythrosine and riboflavin (Vitamin B_2) were interacted with VP/AN hydrogel.

As a result, it can be said that highly swollen VP/AN hydrogels can be used a super water retainer for carrying of some substances in aquatic fields involving environmental, pharmaceutical, agricultural, and biomedical applications.

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