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Radiation Induced Synthesis of 2-Hydroxyethyl Methacrylate-Co-Vinylbenzyltrimethylammonium Chloride Binary Hydrogel System-I: Equilibrium Swelling Studies

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High-energy gamma radiation has been used to synthesize 2-hydroxyethyl methacrylate-co-vinylbenzyltrimethylammonium chloride (HEMA-co-VBT) hydrogels. Unlike pure poly(vinylbenzyltrimethylammmonium chloride) gels, these gels had good strength and could be handled easily. The equilibrium degree of swelling of the gels was a linear function of the VBT content in the gels. The effect of ionic strength, temperature, pH, some solutes of biological importance such as glucose, urea, and surfactants such as Triton-X, Deoxycholic acid, have been reported. An increase in temperature of the swelling medium did not affect the EDS but did affect the rate of swelling of the gels. HEMA-co-VBT hydrogels showed ionic strength responsive properties, and the reversible swelling-deswelling action could be performed in NaCl-water medium for several cycles without losing physical strength of the gel. The gels were also tested for uptake of monovalent anionic dyes namely acid blue 25 (AB25), acid yellow 99 (AY99) from dilute aqueous solutions and found to be suitable for dye uptake with high efficiency.

Keywords gamma radiation, 2-hydroxyethyl methacrylate, vinylbenzyltrimethylammonium chloride, hydrogels, equilibrium swelling

Introduction

Hydrogels are three dimensional crosslinked polymer structures, which are able to swell in the aqueous environment without dissolving or losing their structural integrity (1). The network is often formed by covalently crosslinked polymers, but ionic bonds, crystalline regions, entanglements and Van der Waals forces can also lead to water swellable network materials (2, 3). The water imbibing properties of hydrogels enables them to be employed as a potential device for many applications such as soft contact lenses (4),

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dialysis membranes (5), artificial implants (6), burn dressings (7), drug delivery systems (8), sensors, separation membranes and adsorbents.

The conventional thermo-chemical technique, gamma irradiation or electron beam irradiation has been utilized to synthesize binary or tertiary co-polymer hydrogels to combine the desired properties of all the parent components in the form of an interpenetrating polymer network (IPN) and grafted matrices or random copolymers gels (9–13). Radiation induced synthesis of hydrogels has several advantages over conventional methods viz. high purity products, easy process control, a wide range of synthesis temperatures and the possibility of sterilization during synthesis (14–16). The judicious choice of the components of binary hydrogels can lead to hydrogels that exhibit a combination of unique physiochemical properties, thus permitting their wide-range of applications and often exceptional possibilities for practical applications. For radiation-synthesized gels, gel properties may be programmed by the choice of the main polymer that forms the framework and the co-monomer, its content, and the radiation dose (9–13). Poly(2-hydroxyethyl methacrylate) (PHEMA) based gels have been the subject of interest for scientists and technologists because of their versatile properties, such as biocompatibility, good mechanical strength, high gel fraction, and ease of synthesis. However, low swelling of non-ionic polymer matrix like PHEMA at higher crosslinking extent restricts their applications where high swelling is desired. This problem can be overcome by either functionalization of the base matrix or by co-polymerization with ionic monomers. Apart from the increase in the swelling, introduction of ionic polymers provides stimuli-responsive property against external stimuli like pH, ionic strength, temperature, and electric field, depending on the chemical nature of the ionic polymer (17–20).

In this study, the effect of introducing vinylbenzyltrimethylammonium chloride (VBT), an anion exchange type monomer, on the swelling of PHEMA gel has been investigated. The effect of different swelling medium conditions on the equilibrium swelling of these cationic gels was investigated. These ionic gels were also investigated for uptake of anionic dyes from aqueous solution.

Experimental

Materials

2-hydroxyethyl methacrylate [(HEMA), Mol wt. 130.14] from Aldrich Chemical (purity $>97\%$), was further purified by vacuum distillation at 78°C and 5 mmHg pressure. Only the middle 70% of the distillate was collected. Cuprous chloride was added to the distillation flask to inhibit polymerization during distillation. Vinylbenzyltrimethylammonium chloride [(VBT), Mol wt. 211.74, purity $>99\%$], in solid form, from Fluka Chemicals, anionic dyes namely acid blue 25 (mol wt. 416.39), and acid yellow 99 (mol wt. 496.35) from Aldrich were used as received. All other chemicals used were of AR grade. Double distilled water was used for preparing all solutions and for swelling studies.

Radiation Induced Synthesis of Gels

The gels were prepared by copolymerization of HEMA with VBT in the presence of 30% water. The two monomers were dissolved in water in different ratios, stirred, and filled in glass vials (ID = 1.0 cm, l = 7–8 cm). The vials were deoxygenated under 10^{-3} torr vacuum at liquid nitrogen temperature and sealed. Polymerization was carried out by irradiating the sealed samples at room temperature with gamma rays from a ^{60}Co source

in a gamma chamber GC-5000, supplied by M/s BRIT, INDIA, at a dose rate of 5 $kGyh^{-1}$, as measured by Fricke dosimetry. After irradiation, the glass vials were opened to retrieve polymer/copolymer gels in cylindrical form. The gels samples were rubbery and transparent at room temperature. These samples were cut into 0.5–1.8 mm thick disks with a sharp edged blade and soxhlet extracted with double distilled water to remove residual monomers. Swelling-drying cycles were carried out 3–4 times, and finally the disks were dried under vacuum in an oven at 30°C, and stored in a dessiccator for further use.

Swelling Measurements

The increase in the mass of the samples immersed in aqueous solutions was monitored gravimetrically using Mettler analytical measurements (Accuracy 10 mg) at 26 ± 1°C. Pre-weighed samples were immersed in water, the swelled samples were removed periodically, blotted free of surface water using high quality tissue paper, weighed and returned to the swelling medium. Measurements were taken until the samples reached a constant weight. The swelling ratio and equilibrium degree of swelling (EDS) of the gels were determined using Equations (1) and (2).

$$\text{Swelling ratio} = \text{Swelled weight-Initial weight/Initial weight} \quad (1)$$

$$\text{EDS}(\%) = (\text{Mass of water absorbed by gel/Initial weight}) \times 100 \quad (2)$$

FTIR Studies

Fourier transformed infrared spectroscopy (FTIR) measurements were performed on a FTIR spectrophotometer FT/IR-610 from JASCO, JAPAN. Samples were thoroughly ground at liquid nitrogen temperature and mixed with KBr. The mixture was compressed to prepare disc for FTIR analysis. FTIR spectra were recorded in the range from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} and averaged over 25 scans. Figure 1 shows the

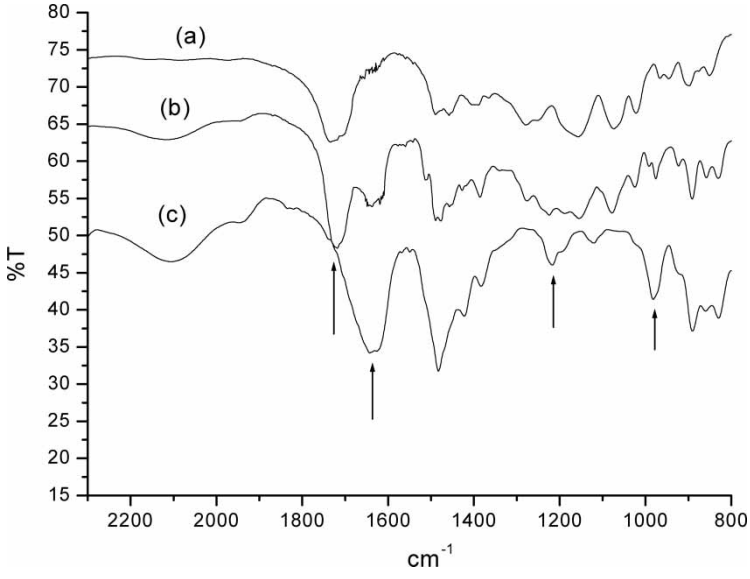
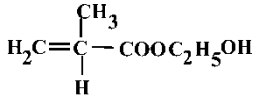


Figure 1. FTIR spectra (a) PHEMA (b) HEMA-co-VBT (HV4) (c) PVBT.

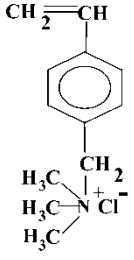
FTIR spectra of PHEMA, HEMA-co-VBT polymer (HV4) and PVBT. The presence of VBT in the HEMA-co-VBT polymer was confirmed by the appearance of extra absorption peaks at 1645 cm^{-1}, 976 cm^{-1} and 1221 cm^{-1} due to C–C stretching, C–H bending of the 1,4-di-substituted aromatic ring and C–N stretching respectively, which was not seen in pure PHEMA sample. The signature of PHEMA in the copolymer gel was confirmed by appearance of peak near 1730 cm^{-1} due to the C=O stretching vibrations.

Results and Discussion

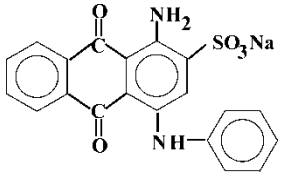
The amount of water absorbed by a hydrogel i.e., equilibrium swelling is a function of (i) hydrophilicity of the polymer (ii) the extent of crosslinking of the network structure (iii) and the number of ionized groups on the polymer. The swelling degree is central to any application of the hydrogel, therefore it is important to examine changes in its swelling degree due to composition of gels as well as due to swelling medium. These studies provide an idea about the water imbibing capacity of the gel matrix in various kinds of swelling environments, which decides its applicability for various applications. Chemical structures of monomers and dyes used in this work are given below.



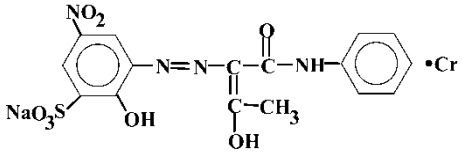
2-Hydroxyethyl methacrylate
(2-HEMA)



Vinylbenzyltrimethylammonium chloride



Acid Blue 25



Acid Yellow 99

Structure of Monomers and Dyes Used for Studies

Effect of Gel Composition

The effect on the extent of swelling of the PHEMA matrix, due to the incorporation of VBT, was investigated by varying the concentration of the ionizable monomer VBT in the feed solution. Table 1 shows the change in swelling extent of the gel with VBT concentration. It can be seen that EDS increased almost linearly with the amount of VBT in the matrix.

When a hydrogel is allowed to swell, water diffuses into the hydrogel and the hydrogel swells and eventually reaches equilibrium. At equilibrium, there are mainly four components of pressures that balance each other and determine the extent of swelling of a hydrogel (21). Equation (3) holds at the equilibrium swelling condition.

$$\pi_{\text{mix}} + \pi_{\text{elast}} + \pi_{\text{ion}} + \pi_{\text{elect}} = 0 \tag{3}$$

where,

π_{mix} = osmotic swelling pressures due to mixing of polymer chains with solvent,
π_{elas} = osmotic swelling pressures due to elastic response to changes in the configuration of the polymer network,
π_{ions} = osmotic swelling pressures due to mixing of ions from solution and from the polymer network,
π_{elec} = osmotic swelling pressures due to changes in the electrostatic interactions of ionized groups upon swelling.

For a non-ionic gel like PHEMA in equilibrium with the solvent, the π_{ion} and π_{elect} components of pressure do not contribute and therefore, the total osmotic swelling pressure is given by Equation (4).

$$\pi_{\text{tot}} = \pi_{\text{mix}} + \pi_{\text{elas}} \tag{4}$$

The parameters π_{mix} and π_{elas} are related to crosslink density and the Flory-Huggins parameter (χ). Thus, the key parameters that determine the swelling of non-ionic gel in a solvent are the crosslink density and Flory-Huggins parameter (χ) (22). If the gels contain ionizable groups, the additional ion related terms π_{ions} and π_{elec} have to be included in Equation (4) (21, 22).

Unlike ionizable polymers, such as poly(acrylic acid), VBT polymers are a highly ionized salt. The similar charged, fixed ions generated on the polymer chains due to

Table 1
EDS of HEMA-co-VBT gels synthesized at a dose rate of 5 kGyh^{-1}

Samples	Dose (kGy)	[HEMA] (mol%)	[VBT] (mol%)	EDS (%)
HV1	6.1	90.75	9.25	669.9
HV2	6.1	80.33	19.67	1809.8
HV3	6.1	68.34	31.66	2824.9
HV4	6.1	55.0	45.0	3440.4
HV5	2.5	68.34	31.66	4068.4

ionization repel each other, and this repulsion tends to stretch polymer chains to an extended state from a closed coiled state, which causes opening of the polymer chains and overall swelling of the hydrogels. Thus, the extent of swelling increases with an increase in the number of ionizable groups in the network. Also, the water binding sites, such as tetra-alkylammonium ions, are known to have a net structure causing effect (23). Their high electric fields not only polarize, immobilize and electrostrict the nearest neighbor molecules, but they also induce additional order beyond the first layer of water molecules. The higher attractive field that can be felt to several layers in the case of—$N^{+}(CH_3)_3$ probably causes many more layers of water associated to the first layer, which is in immediate vicinity of the polymer than in comparison to the OH group in PHEMA and hence, more water uptake is seen in gels containing VBT.

It was also noticed from the results given in Table 1 that the swelling extent of the gels was also a function of total radiation dose imparted to the hydrogel. The swelling being higher for gels synthesized by lower radiation dose (comparing gels HV4 and HV5), indicating the gel was further crosslinked on irradiation in the dose range studied.

Effect of Ionic Strength

For polyelectrolyte hydrogels, the last two pressure terms (π_{ion} and π_{elect}) in Equation (3) contribute significantly and control the swelling of the gels to a greater extent. The Donnan equilibrium theory evaluates the osmotic pressure π_{ion} of the hydrogel system by following Equation (5) (24).

$$\pi_{ion} = RT \sum_{i} (C_i^g - C_i^s) \tag{5}$$

where, C_i is the mobile ion concentration of species i, g and s represent the gel and solution, respectively. This equation indicates that the greater the difference between the ionic concentration inside the gel and in the external solution, the larger the swelling. The ions inside the gel arise from two sources: dissociation of ionic groups bound to the matrix, and ions that diffuse into the gel from the surrounding solution. The concentration inside the gel is typically much higher than the external solution, so π_{ions} is quite high. As a result, water flows into the gel to dilute the ion concentration, causing the gel to swell. As contribution due to π_{ions} is significant in extent of swelling of polyelectrolyte gels, the volume of such gels can change sharply with change in the pH or ionic strength of the surroundings.

The effect of ionic strength on EDS of different cationic hydrogels is presented in Figure 2. It is clear from the figure that EDS of the gels containing VBT decreased in the presence of NaCl in the medium and the effect was more pronounce for gels containing a higher VBT content. The result of swelling of one of the gels (HV5) at different NaCl concentrations, in the range from 0 to 2.5 M, is given in the Figure 2 inset. The copolymer gel was seen to shrink drastically with an increase in NaCl concentration in the swelling medium. In the absence of NaCl electrolyte in the aqueous medium, π_{ion} is much higher due to the large difference in the ionic concentration inside the gel and external solution. When NaCl is added to the swelling medium, the ionic concentration in the medium C_i^s increases, which decreases the ionic concentration gradient ($C_i^g - C_i^s$) and eventually decreases the π_{ions} pressure term, resulting in lower EDS. Secondly, the salt ions in the swelling medium cause the screening of the repulsive electrostatic interactions between ionized groups on the polymer chains and reduces the π_{elect}

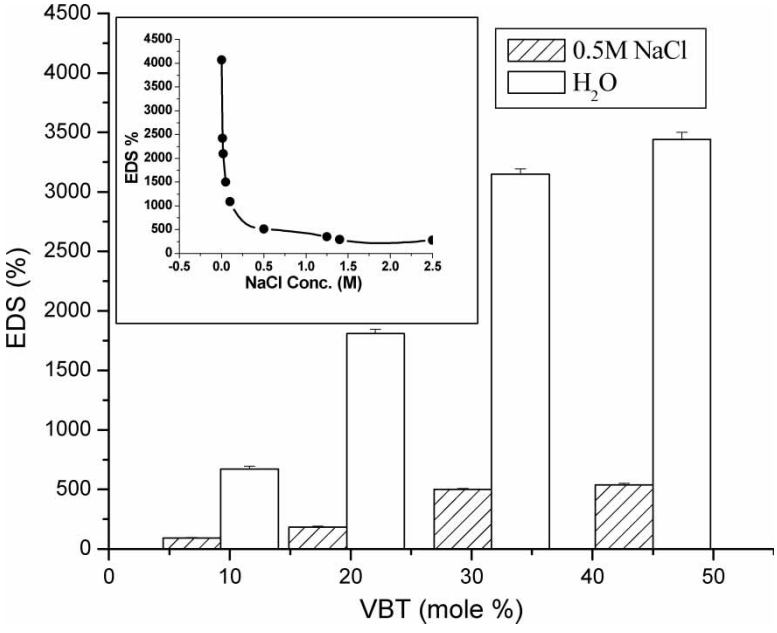


Figure 2. EDS of HEMA-co-VBT hydrogels in water and 0.5 M NaCl solution, dose = 6.1 kGy. Inset: EDS of cationic hydrogel HV5 in aqueous solution of different ionic strength.

pressure term, resulting in coiling of the polymer chains reflected as a decrease in swelling or collapse of the gel.

Figure 3 shows the swelling–deswelling of the gel HV5 when it was allowed to undergo swelling–shrinking by transferring to water and a 0.1 N NaCl solution. It was found that the swelling of gel in water was slower as compared to shrinking in the 0.1 N NaCl solution. The slow swelling may be due to closed pores of the gel in a shrunken state through which water diffusion into the gel matrix is comparatively difficult whereas in the swelled state, the pores are wide open through which water can flow out easily. Also, it has to be mentioned that the changes in the swelling ratio here are not rapid in terms of time, they are only abrupt in the sense that they can be provoked by the presence of NaCl in the medium.

pH Effect on Swelling of Gels

It has been reported that incorporation of a highly ionizable group, such as tetra-alkyl-ammonium chloride or sulphonates results in polyelectrolyte gels relatively insensitive to pH, whereas, introduction of monomers such as acrylic acid produces anionic polyelectrolyte gels whose ionization is a function of pH (25). The effect of pH on the swelling of HEMA-co-VBT hydrogel was investigated in the pH range 1.5–10. The pH of the swelling medium was adjusted in two ways: (i) by using the appropriate amounts of $HClO_4$ and NaOH; (ii) by using KCl + HCl buffer (pH $\sim$ 1.5), Glycine + HCl buffer (pH $\sim$ 3.3), Phosphate buffer (pH 5.8 and 8.8) and Na_2CO_3 + NaOH buffer ($\sim$pH 10.8). The results of these studies are shown in Figure 4. No significant change was observed in the swelling medium where pH was maintained using NaOH or $HClO_4$. However, significant changes in EDS were observed in solutions where the pH was

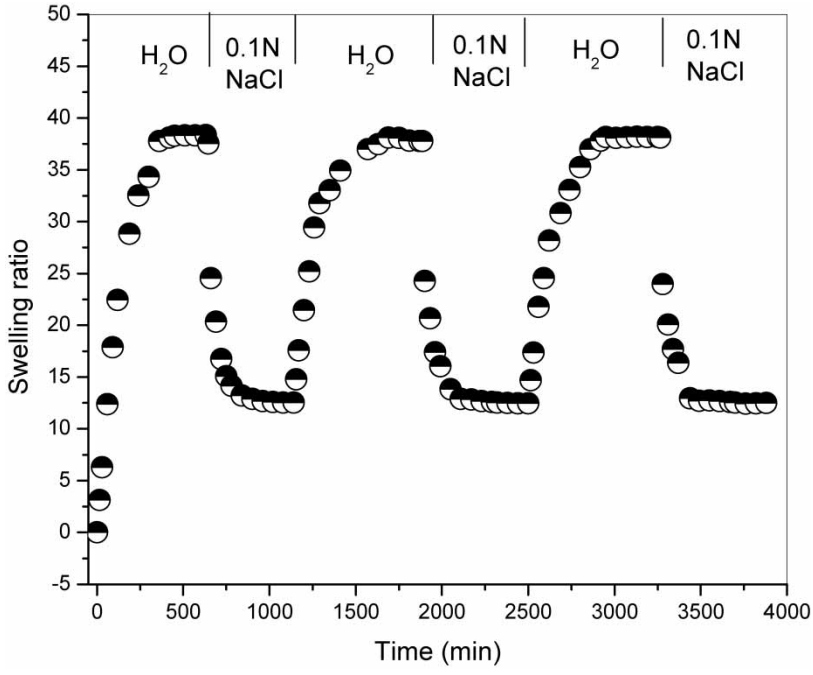


Figure 3. Cyclic swelling-deswelling of hydrogel HV5 in water-NaCl solution.

maintained by buffers solutions, though not following any proper order as shown in Figure 4 insert. This observation clearly indicated that not the pH of the swelling medium, but the ions furnished by the salts used for maintaining the pH controlled EDS of the gels to a great extent.

Effect of Temperature on Swelling Extent and Swelling Rates

The swelling of thermo-responsive polymers, such as poly(N-isopropyl acrylamide) (26), poly(vinyl methyl ether) (27) and others, strongly depends on temperature. As these gels show an abrupt collapse beyond a lower critical solution temperature (LCST). Their abrupt collapse at a critical temperature has been assigned to a critical balance of hydrophobic and hydrophilic groups on the polymer chains (28). At low temperature, strong hydrogen bonding between hydrophilic groups and the surrounding water molecules enables good solubility of polymer in water. However, with increasing temperature, the hydrogen bonding weakens and at temperature $>$LCST hydrophobic interactions become dominant and the refolding of polymer chains causes phase separation of the polymer from the aqueous solution (29).

Poly(vinylbenzyltrimethylammonium chloride) is an amphiphilic polyelectrolyte containing both hydrophobic groups (backbone chain with pendant aromatic ring) and a hydrophilic positively charged quaternary ammonium group in every monomer unit, which ionizes to a polycation in aqueous medium (30). The hydrophobic or hydrophilic interaction may thus dominate depending on external conditions and may cause swelling deswelling of gels. Thus, it was expected that the temperature may affect the extent of swelling of the gels containing VBT and their swelling was studied at

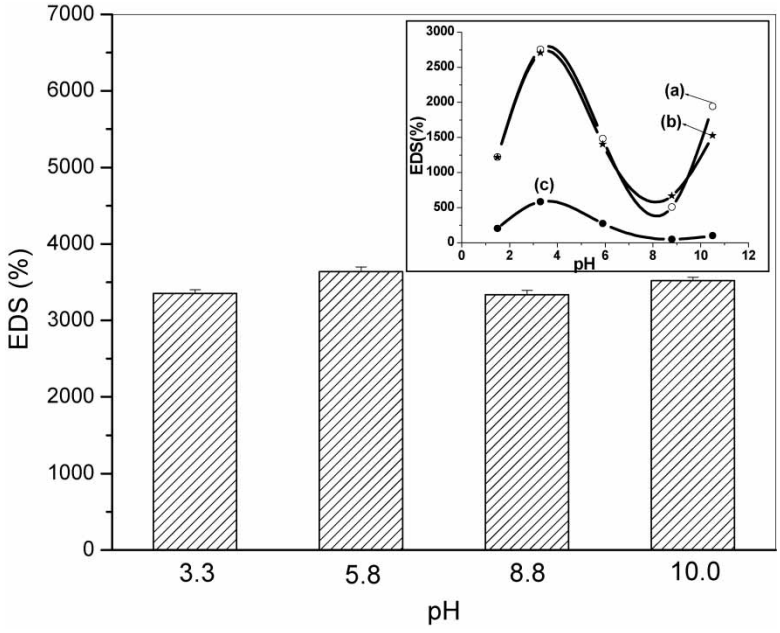


Figure 4. EDS of gel HV5 at different pH maintained using NaOH or $HClO_4$. Insert: EDS of (a) HV4; (b) HV5; (c) HV1 at different pH maintained using buffers.

different temperatures. Swelling of the gels containing different amounts of VBT was studied as a function of temperature in the 28–50°C range. The results are shown in Figure 5, which indicated that there was almost no temperature effect on the EDS of gels. Further, the rate of swelling at different temperatures was evaluated in terms of the penetration velocity (V) of solvent, determined by a weight-gain method as described elsewhere (31). The penetration velocity was calculated from the slope of the initial portion of water uptake curve by following Equation (6):

$$V = (1/\rho A) \times (dW/dt) \tag{6}$$

where dW/dt is the slope of the weight gain vs. time curve, ρ is the density of the solvent, A is the area of one face of the disc.

Figure 6 shows the penetration velocity of gels at different temperatures. It is clear from Figure 6 that the rate of swelling of all gels increased with an increase in temperature of swelling medium and with the increase in VBT content in the gel. Similar observation has been made by other workers for some ionic gels prepared by conventional thermo-chemical, where an increase in rate of swelling was observed with an increase in temperature. However, they have reported that there was an increase in the EDS of gels with temperature (32). Figure 6 shows that the penetration velocity near room temperature for HV5 is lower than HV4 and, as they approach the same penetration velocity values at ~37°C and finally at a higher temperature ~50°C, the penetration velocity of HV5 is greater than HV4. These studies establish that the swelling rate of gels containing more VBT become more affected by temperature. For gels containing the same amount of VBT but prepared at different doses (HV3 and HV5), the less crosslinked HV5 gel,

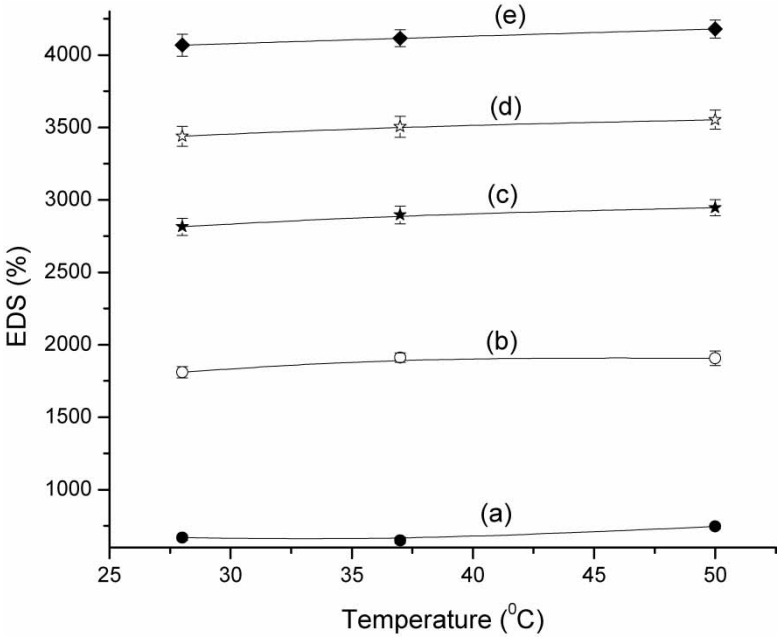


Figure 5. Effect of temperature on the EDS of HEMA-co-VBT hydrogels containing different amounts of VBT (a) HV1; (b) HV2; (c) HV3; (d) HV4; (e) HV5.

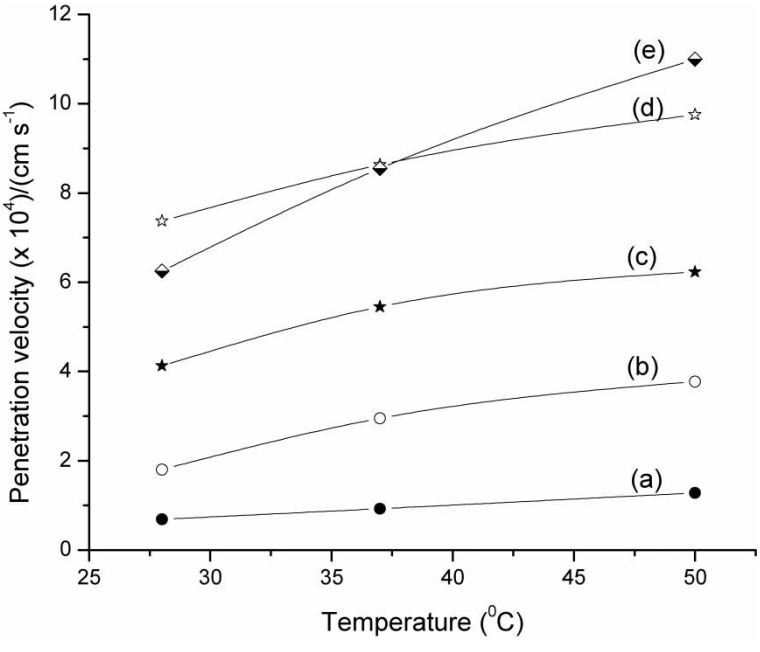


Figure 6. Effect of temperature on the penetration velocity of water in to the HEMA-co-VBT hydrogels containing a different amount of VBT (a) HV1; (b) HV2; (c) HV3; (d) HV4; (e) HV5.

prepared at low total radiation doses, becomes more affected by temperature rise. The latter is probably because of a looser network structure, due to lower crosslinking.

Effect of Solutes on Swelling

The swelling behavior of hydrogels like PHEMA, HEMA-co-NVP (33), HEMA-co-AA (17), HEMA-co-SSS (18), and polyampholytic SSS-co-VBT gels (34) are known to be affected by the presence of solutes of biological interest viz. sodium chloride, urea and glucose. Hydrogels with equilibrium water content (EWC) of around 70% have special significance because of their potential use as extended wear contact lenses, wound dressings, sanitary napkins, and super absorbent baby napkins. Therefore, the effect of various biologically important additives was investigated on HEMA-co-VBT gels with high EDS. The EDS of gel HV5 in various solutions like Glucose, Urea, ionic surfactant deoxycholic acid, non-ionic surfactant Triton-X are shown in Figure 7. It can be seen that EDS of the gel follows the order:

$$\text{DOCA} < \text{Urea} < \text{Glucose} < \text{Water} < \text{Triton-X}.$$

It indicates that the gel shrunk in the presence of all solutes, except Triton-X. The lowest EDS in the presence of DOCA can be explained on the basis of interaction of carboxylic groups of DOCA and the quaternary ammonium group of VBT, causing neutralization and hence, shrinking of the gel to significant extent. The presence of glucose has been shown to shrink non-ionic gels like PHEMA (33), as well as ionic gels such as poly(HEMA-co-*p*-sodium styrene sulphonate) (17). It appears that the presence of glucose causes a salting out effect in swelled gels, due to a concentration gradient resulting in their shrinking similar to the salting out effect of inorganic ions

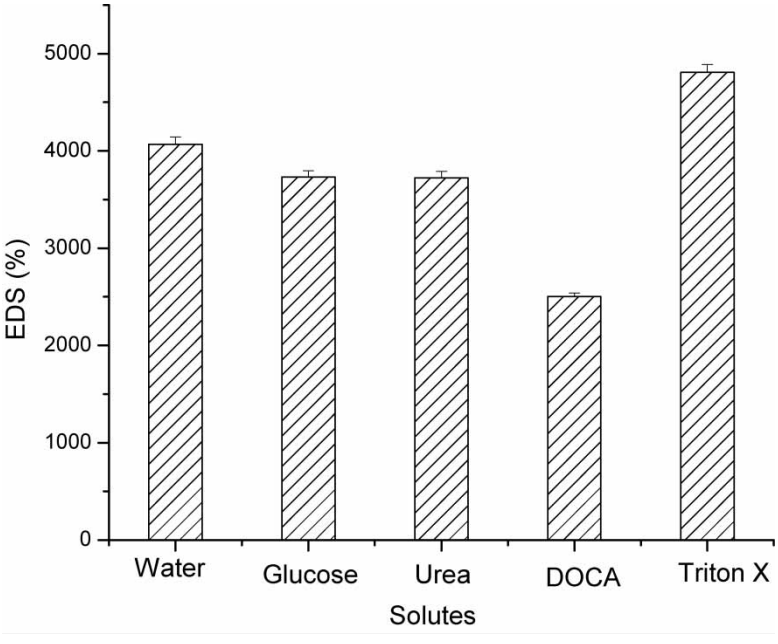


Figure 7. Effect of different solutes on the EDS of HV5 hydrogel.

reported earlier for non-ionic hydrogels (35). However, it was interesting to see that the presence of urea in the medium also shrunk the copolymer gels. The urea is known to further swell PHEMA (36) and other gels (37), explained on the molecular level by proposing the existence of a secondary non-covalent structure based upon hydrophobic interactions between the backbone chains (36, 37). The reverse effect is clearly due to introduction of VBT in the PHEMA backbone. It appears that due to the pendant benzene ring attached to the trialkylammonium group in VBT, the hydrophobic interaction between the backbone of polymer chains are strong enough and are not perturbed even in the presence of urea, which otherwise is well known to reduce the attractive hydrophobic interactions in the gel. The increase in EDS in the presence of Triton-X, which has a long hydrocarbon chain with an hydrophilic end group, indicates that due to the long hydrocarbon chain, the triton molecule is able to dilute the hydrophobic interaction between the chains to some extent and hence causes further swelling of the gel.

Effect of Organic Solvents on Swelling of Gels

The gels are known to exhibit volume phase transition either due to all of the forces, such as hydrogen bonding, hydrophobic interactions, vander Waals forces, or simply due to Coulombic interactions (38). It has been suggested that the Coulombic interactions are stronger in organic solvents than in water, and solvent quality is also poorer than in water with respect to non-Coulombic interactions (39). The swelling of gel HV5 was studied in a series of organic solvents, namely methanol, ethanol, iso-propanol, *iso*-butanol and *tert*-butanol. The results of these studies are shown in Figure 8. It was found that EDS of HV5 gel decreased significantly when immersed in organic solvents,

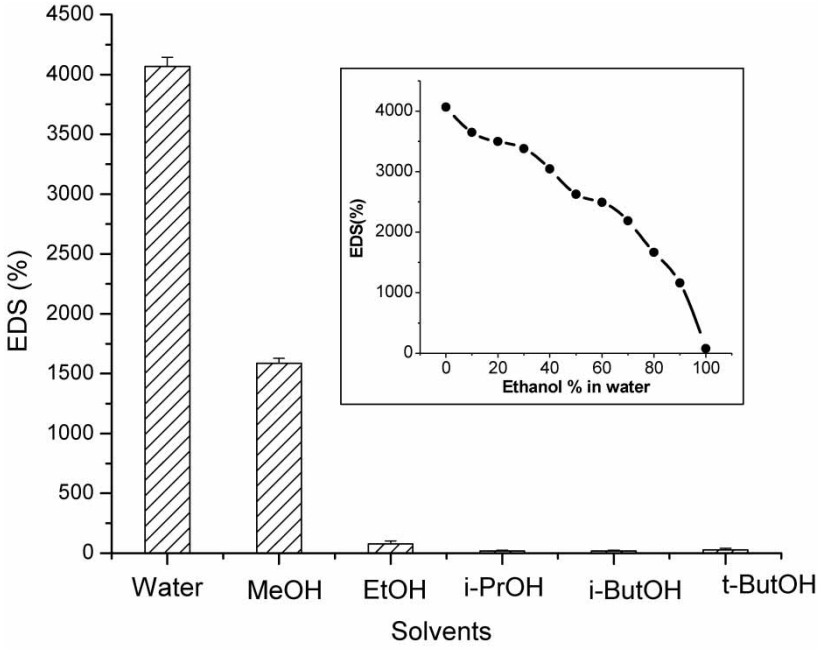


Figure 8. Effect of a different organic solvent on the EDS of HV5 hydrogel. Inset: effect of ethanol concentration on EDS.

such as methanol and ethanol, and the gel collapsed completely in *iso*-Propanol, *iso*-Butanol and *t*-Butanol. Three main forces which govern the swelling or collapse of the polymer network, have been identified as rubber elasticity, the polymer-polymer affinity and the hydrogen ion pressure (40). The balance of these forces is easily perturbed by the matrix composition and external factors such as temperature, type of solvent, etc. It is clear from the results in Figure 8 that polymer-polymer affinity is favored as the swelling medium becomes increasingly hydrophobic. In order to understand this observation further, the swelling of this gel was studied in a water-ethanol mixture. The EDS was seen to decrease with an increase in content of ethanol in the mixture as shown in the Figure 8 inset. In a water-ethanol mix solvent, the EDS of the gel decreased gradually with the increase in ethanol content; the reason may be an increase in the hydrophobicity and a decrease in the solvent quality of the swelling medium for the gel.

Swelling of Gels in Dye Solutions

Polyelectrolyte gels of VBT, due to their anion exchange capability, can act as an effective anion exchange vehicle. However, pure VBT gels, because of their very high water uptake capacity, have poor strength and dimensional stability. The copolymer of VBT with HEMA results in gel with good swelling, as well as better strength, which are easy to handle and can uptake anionic dyes. The copolymer gels were investigated for uptake of mono-valent anionic dyes, namely AB25 and AY99, from aqueous solution. In order to investigate the swelling and adsorption of anionic dyes, gels were allowed to swell in dye solutions of concentration 40 ppm until they reached their equilibrium swelling. After acquiring EDS, the swelled hydrogels showed dark dye colors due to their adsorption.

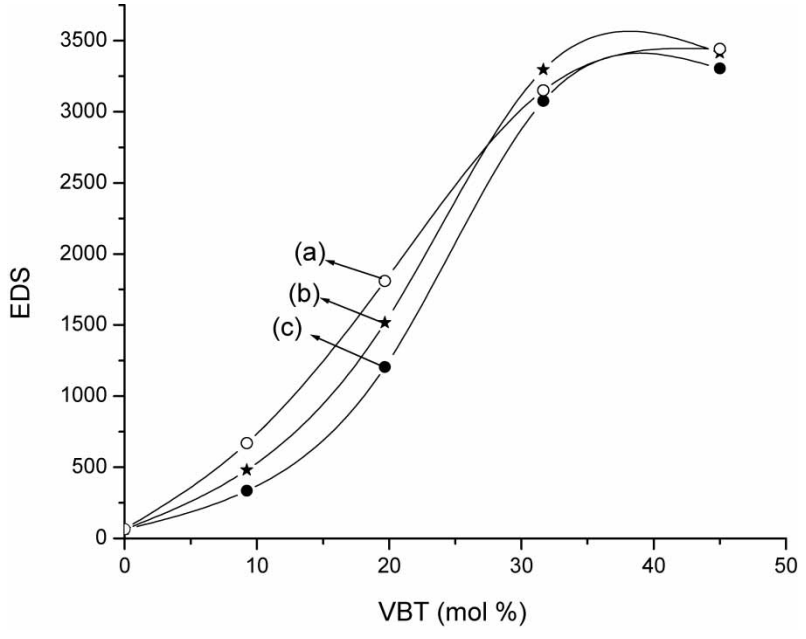


Figure 9. Swelling of HEMA-co-VBT hydrogels in dyes (a) water; (b) AY99; (c) AB25.

In the batch adsorption process at equilibrium, total dye concentration (C_T, mol L^{-1}) is given by Equation (7):

$$C_T = C_B + C_R \tag{7}$$

Where, C_B (mol L^{-1}) is the equilibrium concentration of dye bound to the adsorbent (bound dye concentration) and C_R (mol L^{-1}) is the equilibrium concentration of dye remaining in solution. The value of the bound dye can be obtained from the above equation and is conveniently expressed in terms of binding ratio, r_B defined as Equation (8) (41).

$$r_B = C_B/C_P \tag{8}$$

Where C_P is the base mol (moles of monomer units/liter) $C_P = W_p/M_p$, where W_P is the weight of the polymer gel and M_P is the molecular weight of the repeating units of the polymer. Thus, r_B represents the average number of dye molecules bound to each monomer unit at that free solute concentration.

For a dye molecule to become bound to a hydrogel, it has to diffuse with water into the hydrogel and then bind to oppositely charged sites through ionic interaction. These dyes were only held through ionic interaction was confirmed by the fact that pure PHEMA matrix didn't show any affinity for any of the dyes. As the dye binds to the hydrogel the degree of ionization of the hydrogel changes and so does the EDS. EDS of different gels containing varying amount of VBT in different dye solutions are presented in Figure 9. It is interesting to see that though the dyes also caused charge neutralization in gel their uptake did not decrease the EDS drastically. It may be due to the water binding sites available on the dye molecules itself; the expected decrease in EDS

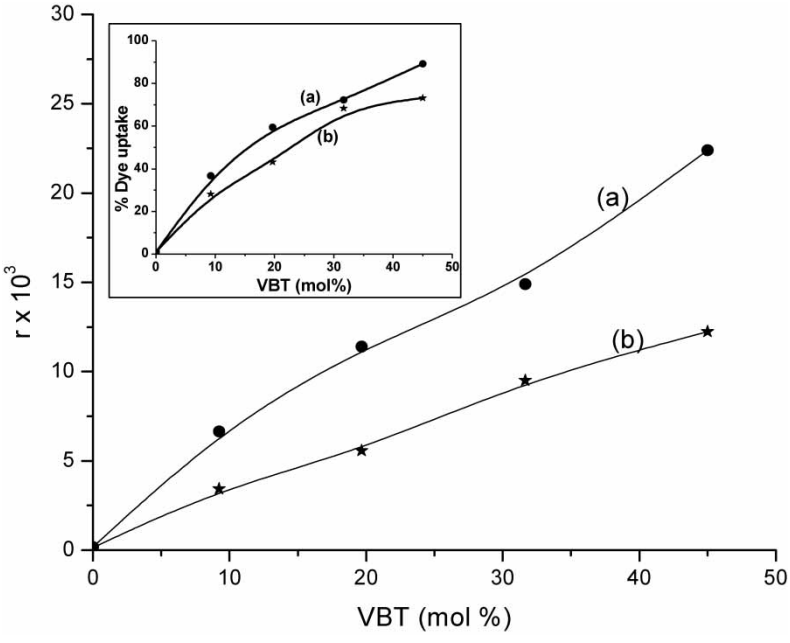


Figure 10. Binding ratio of dyes for HEMA-co-VBT hydrogels as a function of VBT content (a) AB25; (b) AY99. Inset: % dye uptake by different gels as a function of VBT content (a) AB25; (b) AY99.

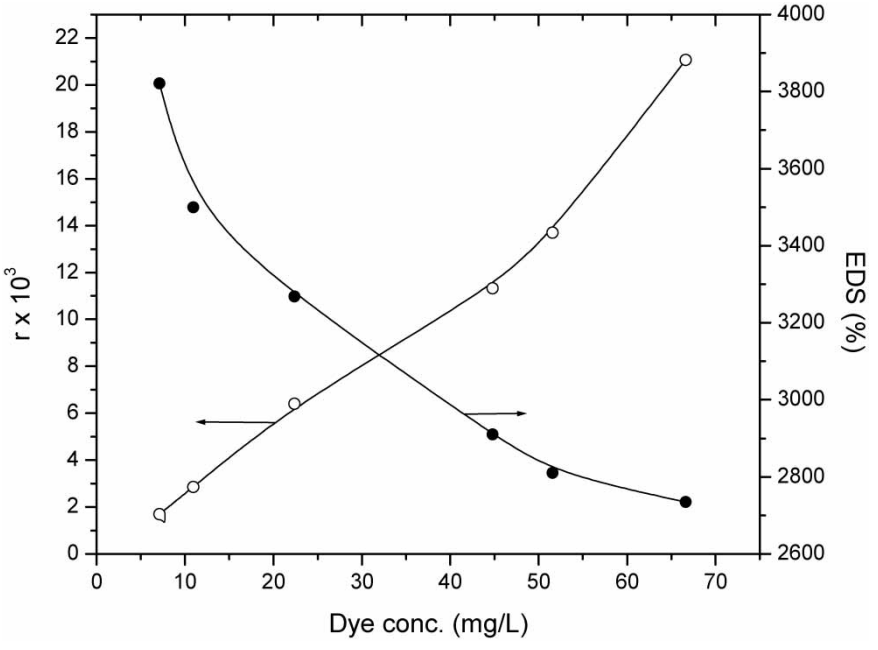


Figure 11. Binding ratio and EDS of dye AB 25 on HEMA co-VBT hydrogel HV5 as a function of initial dye concentration.

because of charge neutralization was compensated by water binding sites available on the dye molecule. The EDS in AB25 solution is lower than that in AY99 solution for all the gels. The binding ratio of these gels was also determined for both the dyes as shown in Figure 10. The results indicate a more efficient binding of acid blue 25 in comparison to AY99, which is also supported by the EDS data. This indicates some role of the chemical structure of dye molecule in binding of the dye to the gel. Figure 10 (inset) shows the percentage dye uptake by a series of gels as a function of VBT content in the gel. It was found that the percentage removal of dye increases with the increase in the VBT content. The removal of AB25 is more efficient than that of AY99 for the series of gels. In order to see the binding of dye as a function of dye concentration, gel HV5 as a representative gel was used for binding of AB25 dye in the concentration range between 5 to 70 ppm. Results of these studies are shown in Figure 11, which showed that the higher the dye concentration, the higher is the binding of the dye in the concentration range studied and lower is the EDS.

Conclusions

From equilibrium swelling studies of HEMA-co-VBT hydrogels, it can be said that the introduction of anion exchange type of monomer VBT into PHEMA changes its EDS significantly. The EDS of these gels decreased significantly when the gels had some ionic interaction with the swelling medium. The rise in temperature of the swelling medium only increases the rate of approach to EDS and not the EDS. The HEMA-co-VBT hydrogel showed ionic strength responsive property and the swelling deswelling of the gels can be performed in water-NaCl solution for many cycles without affecting the

shape and strength of the gel. These gels can be used as an efficient vehicle for dye removal from dilute dye solutions.

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