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Thermal Stability and Swelling Behaviour in Aqueous Medium of Acrylamide Based Hydrogels

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ABSTRACT

Swelling behaviour of acrylamide-N,N'-methylene-bis-acrylamide (copolymer) hydrogel was investigated at 281K, 293K, and 303K in aqueous solutions. Amount of swelling of hydrogels increases with time, and ultimately an equilibrium volume swelling is attained. The extent of swelling of the gels prepared in a homogenous medium depends on temperature, whereas those prepared in a heterogeneous medium are less temperature dependent, indicating the formation of a highly crosslinked, tighter network structure, as also supported by the Differential Scanning Calorimetry (DSC) study. Diffusions of water were studied, and the values of the diffusional exponent were found to fall in the range between 0.45 and 0.5, indicating a Fickian type of diffusion in nature. Thermogravimetric study indicates that most of the gel samples are thermally stable up to 473K and achieve more thermal stability with more crosslinking when prepared in heterogeneous medium polymerisation.

Keywords: *Acrylamide; Hydrogel; Crosslinker; N,N/-Methylene-Bis-Acrylamide; Polymer Swelling; Redox Initiator*

Introduction

Hydrogels are hydrophilic-natured three-dimensional networks and have been used in medicine, bioengineering, biotechnology, pharmacy, the food industry, agriculture, photographic technology and other fields. Swelling properties of acrylamide-based hydrogels are very much responsible for their various uses, such as controlled release applications for delivery of enzymes, hormones, contraceptives, anticoagulants, etc. (Caykara *et al*., 2006; Elvira *et al*., 2002). The gel swelling phenomenon has been the subject of numerous studies in polymer physics (Flory, 1953). It has been observed that the minute changes in the external conditions, such as temperature, solvent composition, ionic strength, and external electric field, can induce drastic changes in the gel swelling network (Tanaka, 1978; Tanaka *et al*., 1980; Ricka & Tanaka, 1984; Tavakoli *et al*., 2006; Hirotsu, Hirokawa & Tanaka, 1987). In particular, it is well established that under certain conditions, polyelectrolyte gels may undergo a discontinuous volume change during swelling (Hooper *et al.*, 1990; Joanny & Leibler, 1990). Therefore, investigations of the swelling behavior of acrylamide-based hydrogels are very much interesting and have been reported repeatedly during the last four decades. The swelling property, which depends on the network structure, is intimately related to the conditions under which the polymer gels were formed (Dusek, 1982; Yürüksoy, 2000). In both academic studies and industrial applications, acrylamide hydrogels were obtained by the free radical copolymerisation of acrylamide (AM) and N,N/-methylene-bis-acrylamide (Bis) using various initiator systems. Recently, hydrogels of AM – Bis copolymer have been synthesised using Fe(III)/thiourea (TU) and Ce(IV)/TU redox initiator systems in a homogeneous aqueous medium and also in the interlayer spaces of the vermiculite heterogeneous microenvironment (Debnath, Bit & Saha 2009). It was noticed that the interlayer space of vermiculite offers a novel reactor resulting in a dramatic change of polymerisation kinetics in which the linear termination process is hindered apparently due to the failure of the growing polymer chain to transfer electrons to the metal ions and consequently a high molecular weight polymer with high reaction yield results (Debnath, Bit & Saha, 2010a; Debnath, Bit & Saha, 2009). In the case of vermiculite medium polymerisation, the Fe(III) ions are preloaded into the intercalated spaces of vermiculite, a smectite, to produce FeV composites prior to the polymerisation reactions (Debnath, Bit & Saha, 2010b). In this article, we have studied some physicochemical characteristics like swelling and thermal properties of synthesised hydrogels and observed that the hydrogels apparently behaved as superabsorbent gels.

Experimental

Materials

Hydrogels of AM and Bis are prepared using Fe(III)/TU and Ce(IV)/TU redox initiator systems in homogeneous and heterogeneous media (vermiculite), following the method described elsewhere (Debnath, Bit & Saha, 2009).

Experiments of Swelling

The swelling behaviour of AM-Bis hydrogels was studied using a glass (Pyrex) apparatus designed purposefully as shown below in Figure 1, in which a graduated horizontal tube of 2 mm diameter (CD) is attached with a 'U' tube by standard joint connector at 'C'. One arm of the 'U' tube contains a sintered glass (B) (Borosil(R), Porosity Grade 1, Pore Size 90-150 microns) of 20 mm diameter fitted horizontally in a vertical crucible (A) in the same level of the graduated tube. Other end of the graduated tube is made funnel-like (E) in order to help with pouring water for the swelling experiment. During the running of the experiment, distilled water was filled up in the 'U' tube and the graduated tube up to the zero mark (D). The graduated tube is always kept horizontal, and the water level in the U-tube just touches and wets the sintered glass at the beginning.

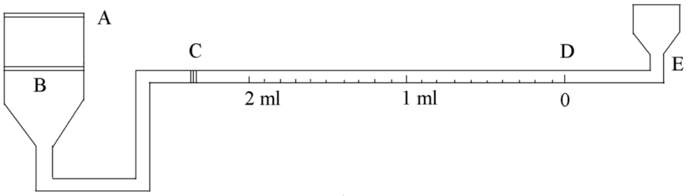

Figure 1: Swelling Apparatus

The system was maintained at a constant temperature using a water bath, keeping the two open ends of the apparatus in air above the water level of the bath. Accurately weighed (0.1 gm) gel sample in powder form is taken in the sintered glass crucible, and immediately the water content in the graduated tube starts decreasing due to the swelling of the hydrogel. Volume of water absorbed was measured directly after a definite time interval, and the percentage of water (S) absorbed by the hydrogel was calculated and plotted as a function of swelling time.

Experiments of Thermal Stability

The thermal stability of the hydrogels prepared under various conditions was analysed by thermogravimetry (TGA) performed from room temperature to 773K in air (rate of heating is 5K per minute).

Differential Scanning Calorimetry (DSC) was performed by a Perkin-Elmer (Pyris-6) system (rate of heating 5K per minute) to understand the behavior of polymers, like the softening temperature and glass transition temperature of dry and moist hydrogels.

Results and Discussion

The percentage of water $(\%S)$ absorbed by the hydrogels was calculated by using the following expression

$$\%S = \left[\left(V_0 - V_t\right)/M_p\right].100 = \left(S_w/S_p\right).100 \qquad [1]$$

$$[\text{Assuming } V_0 - V_t = S_w \text{ and } M_p = S_p]$$

Where *V*0 is the initial water volume in the zero position of the graduated tube. *V t* is the final water volume in the graduated tube after time 't' in minutes. *Mp* is the weight of the gel particle in the dry condition.

Effect of Crosslinker Concentration on Swelling

Throughout the present study 'crosslinker (Bis) concentration' indicates the percent concentration of Bis in the AM and Bis monomer mixture in the reaction medium during polymerisation. The effect of Bis concentrations on the swelling behaviour of hydrogels is shown in Figure 2. In this experiment the crosslinker concentration was varied between 2 mol % and 14 mol %. Total monomer concentration (AM + Bis) was maintained at 0.4 M. Initially the rate of swelling is increased steadily but ultimately assumes a steady value.

However, with the rise of crosslinker concentration, decrease in swelling is noticed. It may be attributed to the fact that as the crosslinker concentration is increased, the molecules of the crosslinker occupy positions between the chains of monomers that lead to more rigid network structure. With increase in the crosslinker concentration, the composition of the hydrophilic group (i.e., amide group of polyacrylamide) in the resulting gels decreases, which leads to a lowering in the percent swelling, a fact which is also reported earlier (Buckley, Berger & Poller, 1962).

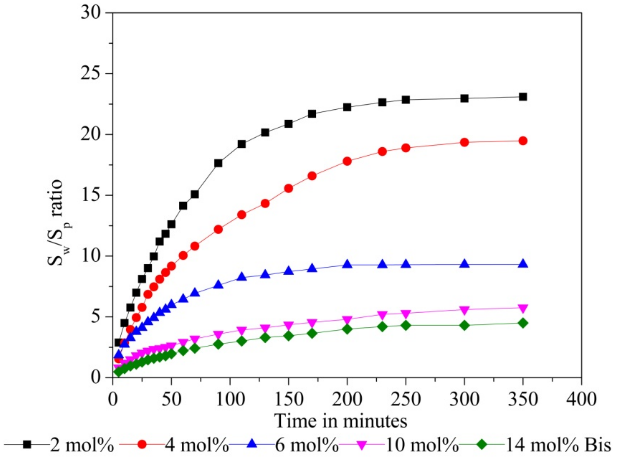

Figure 2: Variation of Swelling Ratio with Time of Hydrogels Prepared with Various Amount of Crosslinker by Fe(III)/TU Redox Initiator Systems at 303K

Table 1 depicts the equilibrium volume swelling [*%S(V)*] of the hydrogels prepared at different temperatures with different Bis percentage. It is obvious from the table 1 that *%S(V)* decreases with rise in Bis percentage in the AM-Bis monomer mixture at a particular temperature and also increases with a rise in temperature for particular hydrogels. With the increase in crosslinker, the network structure becomes more and more rigid, and water molecules can't diffuse easily into the network.

Table 1: Equilibrium Volume Swelling [%(SV], Diffusion Constant (K), and Swelling Exponent (n) of Hydrogels Prepared Under Various Experimental Conditions

Sample no	Bis(mol%)	Temp (K)	*%S(V)*	Diffusion Constant (*K*)	Swelling Exponent(*n*)
1	2	303	2400	0.0311	0.501
2	4	303	2010	0.0321	0.573
3	6	303	930	0.0935	0.489
4	10	303	576	0.0757	0.458
5	14	303	457	0.0493	0.547
6	2	293	1982	0.0972	0.485
7	4	293	1485	0.1064	0.493
8	6	293	846	0.1108	0.523
9	10	293	448	0.1130	0.534
10	14	293	458	0.1097	0.499
11	2	281	1782	0.0837	0.499
12	4	281	814	0.0934	0.493
13	6	281	721	0.0982	0.485
14	10	281	325	0.0880	0.487
15	14	281	300	0.1033	0.476

Effect of Temperature

The swelling behaviour of the AM-Bis hydrogel samples was examined at three different temperatures (i.e., 281K, 293K, and 303K). Amount of swelling of hydrogels (*/wpSS*), prepared in homogeneous medium, increases with the rise in temperature. But, for the vermiculite medium hydrogels, the gel swelling varies little with temperature. The variation of gel swelling of 2 mol % Bis with temperature for homogeneous and heterogeneous media is shown in the Figure 3 (other compositions are not shown here). The gels prepared in vermiculite medium are less swellable, as shown in the figures, which indicate the formation of tighter network structure in the presence of more crosslinking in the sample.

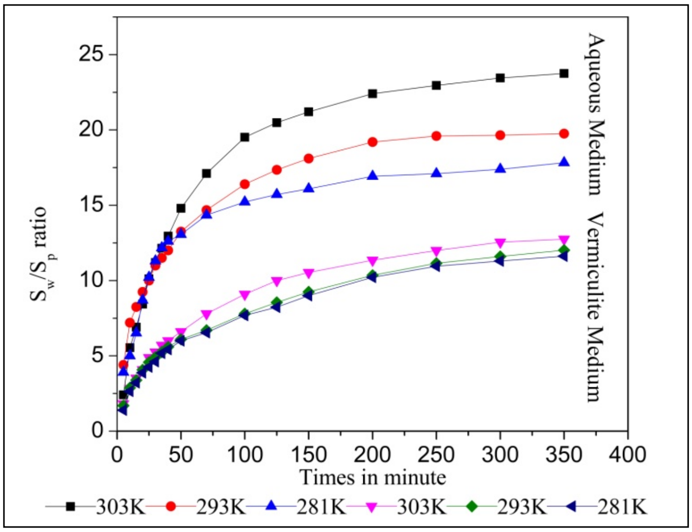

Figure 3: Variation of Swelling Ratio with Time of AM-Bis Hydrogels (2 mol % Bis) Obtained in Homogeneous Medium and in Vermiculite Medium at Various Temperatures

Diffusion of Water

Water molecules diffuse into the glassy hydrogels when brought in contact with water and swell. Diffusion induces water migration into pre-existing or dynamically formed spaces between hydrogel networks. Swelling of the hydrogel leads to larger-scale segmental motion, resulting in an increased distance of separation between hydrogel chains. The mechanism of water diffusion in swellable polymeric systems has received considerable attention recently because of the important applications of swellable polymers in the biomedical, pharmaceutical, environmental, and agricultural engineering fields, as has already been mentioned. In the case of drug delivery systems, Fick's law of diffusion provides the fundamental description of solute transport processes from polymeric matrices.

The following equation is used to determine the type of diffusion process of water into hydrogels (Peppas & Franson, 1983; Xue, Champ & Huglin, 2001).

$$F = (M_t / M_i) = Kt^n \quad [2]$$

$$ln(M_t / M_i) = lnK + n.ln(t) \quad [3]$$

Where *Mt* and *Mt* represent the amount of solvent diffused into the gel at time '*t*' and at infinite time, respectively. '*K*' is called Diffusion constant, related to the structure of the network, and the exponent '*n*' is Swelling Exponent or Diffusional Exponents which is a number to determine the type of diffusion.

The slope and intercept of the line obtained by plotting *In*(M_t/M_t) versus *In*(*t*) gives the values of *n* and *K*. There are three types of diffusion depending on the relative rates of diffusion and polymer relaxation. The first one is Fickian type diffusion (*n*= 0.45 to 0.5), in which the diffusion rate, R_{diff} is clearly slower than the relaxation rate of polymer chains, R_{relax} ($R_{diff} << R_{relax}$). Here the swelling is controlled by the diffusion of water into the polymer. Fickian diffusion refers to the solute transport process where the polymer relaxation time (t_r) is much greater than the characteristic solvent diffusion time (t_d). The second one is Case II diffusion (*n*= 1.0), where the diffusion of water is very rapid compared to relaxation of polymer network ($R_{diff} >> R_{relax}$). The third class is non Fickian type or anomalous diffusion where ($R_{diff} \approx R_{relax}$). Here is the value of '*n*' in the range $0.5<n<1.0$, where both the diffusion of water and the relaxation of polymer network control the overall rate of water uptake. Equation 3 is applied to the initial stages of swelling (up to 60% swelling), the *n* and *K* values were calculated from the slopes and intercepts of the lines, respectively.

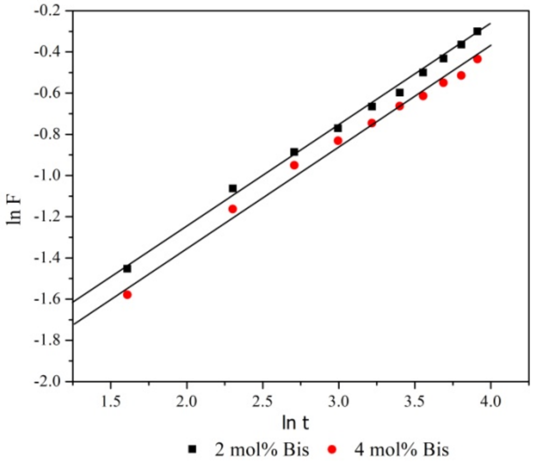

Figure 4: The Typical Curves of Swelling Kinetics of AM-Bis Hydyogels at 293K

The values of diffusion constants and diffusional exponents of all respective hydrogels are calculated and tabulated in Table 1, and a representative plot is shown in Figure 4. The values of diffusional exponent, *n* have been found to be in the range between 0.45 and 0.5, where a swelling constant, *K* varies between 0.0311 and 0.1130. Therefore, the diffusion of water into hydrogels may be considered as a Fickian type. This behavior is generally explained as a consequence of a slow diffusion rate, R_{diff} of the polymer matrix with respect to the relaxation rate of the polymer chains,R_{relax} (Peppas & Franson, 1983). Taking into account this diffusion type, the present hydrogels can further be studied for the controlled delivery of different drugs in future.

Thermogravimetric Analysis (TGA)

Thermograms of dry hydrogel samples, prepared under homogeneous solution conditions (in absence of vermiculite) by $FeCl_3$/TU initiators, are shown in Figure 5. In general, the thermograms display multistage weight loss features as a function of temperature. However, the samples are completely decomposed/charred at about 673K. For almost all the samples, weight loss started at around 473K. The maximum weight loss region lies between 523K to 673K, except for the sample with 4 mol % Bis, and it shows substantial weight loss at 473K. It was observed that the midpoints of this region (inflection point, TGm) vary substantially with crosslinker concentration. As the concentration of crosslinker is increased from 4 mol % (with respect to total monomer concentration) to 10 mol %, the thermal stability increases due to increase in the crosslinking network. However, it is interesting that 2 mol % of crosslinker gives the highest stability.

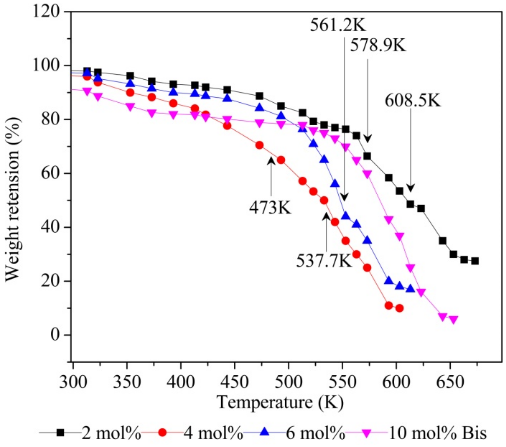

Figure 5: Thermal Behavior of Dry Hydrogels Prepared in Absence of Clay at 323K Using Fe(III)-TU Initiating System: $FeCl_3 = 1.5x10^{-3}$ M, TU = 0.04 M

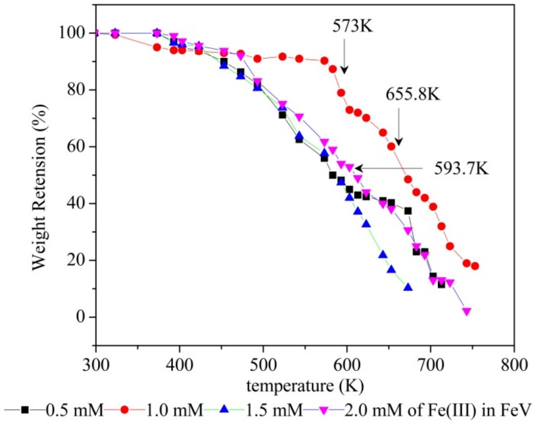

Figure 6: Thermal Behavior of Dry Hydrogels Prepared in Presence of Clay at 323K Using FeV-TU Initiating System: TU = 0.04M. Bis = 4 mol %

Figure 6 represents the thermograms of dry hydrogel samples prepared by FeV-TU redox initiator systems with variable FeV concentrations. It is also observed that although thermal stability of hydrogels, in general, increases with FeV concentration during polymerisation, maximum stability is displayed by an intermediate FeV concentration of 1.0 mM (FeV concentration indicates the concentration of Fe(III) in FeV). It is also interesting to note that only minor weight loss is observed up to 423K for all the samples except that prepared in presence of 1.0 mM FeV. This particular sample is thermally stable up to 573 K, and weight loss starts above this temperature. If attention is focused on the characteristic features of each thermogram of acrylamide hydrogel, it gives a clear impression that during decomposition of polyacrylamide in the course of heating, the non-stoichiometric loss of water takes place, followed by subsequent loss of ammonia and other gaseous products from the polyacrylonitrile structure formed, along with those from the remaining polyacrylamide (Iwahara *et al.*, 2000).

Differential Scanning Calorimetric (DSC) Study

The DSC profile (Figure 7) show endothermic peaks at 330K, 343K and 338K that indicates the presence of glass transition for the hydrogels having 2 mol %, 6 mol % and 10 mol % Bis concentrations respectively.

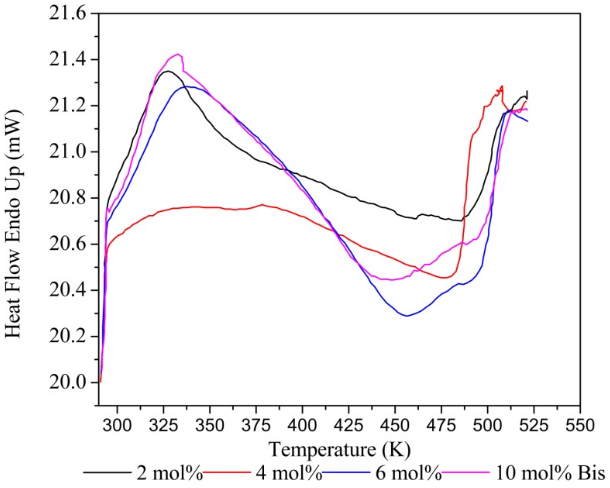

Figure 7: DSC Curve of Dry AM - Bis Hydrogel Prepared in Clay Medium: Fe(III) in FeV = 1.5 mM, TU = 0.04 M, Temp= 323K

The DSC profiles also display the characteristic temperature where softening of the copolymer starts. The onset of softening temperature occurred for the above three samples at 493K, 488K and 498K respectively. Previous workers have reported different values of glass transition temperature and softening temperature for polyacrylamide homopolymer and copolymer samples (Greenberg & Kusy, 1980). Unlike all other samples, the copolymer having 4 mol% Bis concentration, however, shows a DSC profile with a broad endothermic band (centred at 353K) instead of a well-defined peak. However, the softening temperature at 483K is fairly well defined.

Figure 8 shows DSC profiles of hydrogel samples under moist conditions (i.e., gel phase), prepared in different experimental conditions with varying amounts of FeV concentrations. Two types of moist gels are collected for DSC study: one is low FeV content hydrogels (which are collected from the upper portion of the sample vessel after polymerisation with FeV), and another is high FeV content hydrogel (which is collected from the lower portion of an unstirred suspension after polymerisation with FeV). The techniques of the polymerisation process were discussed elsewhere (Debnath, Bit & Saha, 2010a; Debnath, Bit & Saha, 2010b). The endothermic peaks at different temperatures are displayed by samples and ranged between 383K to 433K for loss of water. However, interestingly, the endothermic peaks displayed by these samples are actually overlaps of three closely separated peaks in each case, indicating three different potential sites for water retention in the acrylamide hydrogels. Water retention characteristics of the hydrogel may be discussed in terms of DSC endothermic peak positions as well. Endothermic peak temperatures on the DSC profiles clearly manifest the water binding power of the hydrogel samples. Hydrogels prepared in the presence of 1.5 x 10^{-3} M Fe(III) in FeV displayed the highest water removal temperature, indicating strongest bond with water molecules. The enthalpy change associated with the endothermic phase change of hydrogels under moist conditions varies from 2398 J/g to 4433 J/g. The enthalpy change for the samples is plotted as a function of concentration of Fe(III) ions in FeV in Figure 9, which shows that the profile passes through a maximum for the samples prepared at 1.5 x 10^{-3} M Fe(III) ions in FeV concentration.

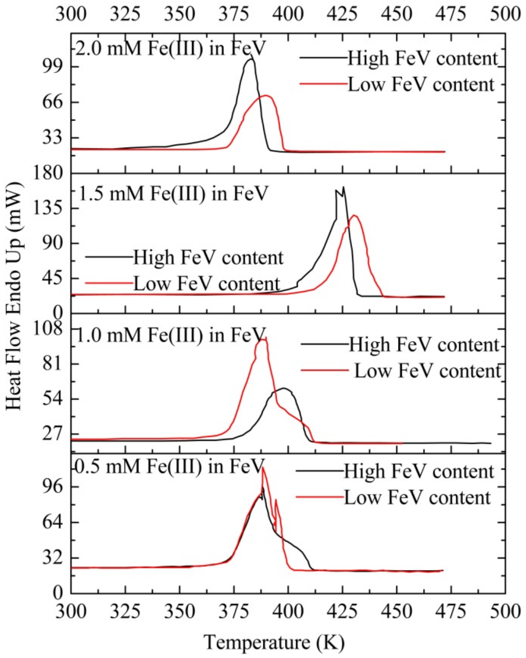

Figure 8: DSC Curve of Moist AM-Bis Hydrogel Prepared in Clay Vermiculite Medium: Bis = 4 mol%, Fe(III) in FeV = 0.5 mm to 2 mm, TU = 0.4M, Temp = 323K

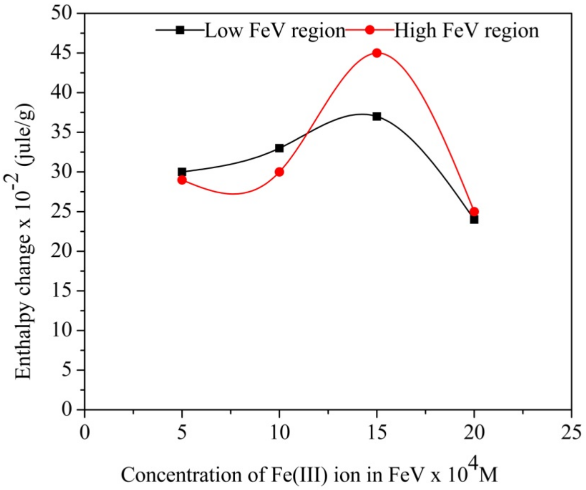

Figure 9: Enthalpy Change as a Function of Concentration of Fe(III) Ion in FeV

This indicates that the water molecules are strongly bonded with the network structure of the gels that are prepared in the presence of 1.5 x 10-3 M Fe(III) ions in the vermiculite mineral (TU = 0.04 M, Bis = 4 mol %).

Conclusion

The present method of measuring the swelling property of hydrogel samples is found to be simple, reproducible and accurate, whereas previous methods of measuring swelling were error-prone (e.g., blotting and weighing). The hydrogel prepared by Fe(III)/TU redox system can be termed a supergel because of its high water-absorbing capacity. High crosslinking may be achieved in vermiculite heterogeneous phase reaction, leading to more rigid network formation. The process of swelling in each case is found to be of the Fickian type.

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