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Study on swelling of hydrogels (PAAm) at various temperatures by using fluorescence technique

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Abstract Steady-state fluorescence (SSF) technique was employed for studying swelling of polyacrylamide (PAAm) hydrogels. Disc-shaped gels were prepared by free-radical crosslinking copolymerization of acrylamide (AAm) with *N*, *N*′- methylenebis (acrylamide) (BIS) as crosslinker in the presence of ammonium persulfate (APS) as an initiator. Pyranine was introduced as a fluorescence probe. Fluorescence intensity of pyranine was measured during in situ swelling process at various temperatures and it was observed that fluorescence intensity values decreased as swelling is proceeded. Li–Tanaka equation was used to determine the swelling time constants, τ_c and cooperative diffusion coefficients, D_c from intensity, weight and volume variations during the swelling processes. It is observed that swelling time constants, τ_c decreased and diffusion coefficients, D_c increased as the swelling temperature is increased. The swelling activation energies, ΔE were measured from the intensity, weight and volume variations and found to be 10.7, 32.2 and 64.1 kJ mol^{-1}, respectively.

Introduction

Hydrogels are important materials of both fundamental and technological interest. They are usually prepared by free-radical cross-linking copolymerization of a monovinyl monomer with a divinyl monomer (as cross-linker) in a homogeneous solution. In recent years, hydrogels have received considerable attention for use as specific sorbents and as support carriers in biomedical engineering. Investigations of the swelling behavior of hydrogels have been researching during the last decade. Volume phase transitions in gels may occur from dry to swollen states either continuously, or by sudden jumps between them [1, 2]. The equilibrium swelling of gels in solvent has been extensively studied [3–5]. The swelling process of chemically cross-linked gels can be understood by considering the competition between the osmotic pressure and the restraining force [6–10]. The total free energy of a chemical gel consists of bulk and shear energies. In fact, in a swollen gel, the bulk energy can be characterized by the osmotic bulk modulus *K*, which is defined in terms of the swelling pressure and the volume fraction of a polymer at a given temperature. On the other hand, the shear energy that keeps the gel in shape can be characterized by shear modulus *G*. Here, shear energy minimizes the non-isotropic deformations in the gel. The theory of kinetics of swelling for a spherical chemical gel was first developed by Tanaka and Filmore [11], where the assumption is made that the shear modulus *G* is negligible compared to the osmotic bulk modulus. Latter, Peters and Candau [12] have derived a model for the kinetics of swelling in spherical and cylindrical gels by assuming non-negligible shear modulus. Recently, Li and Tanaka [6] have developed a model where the shear modulus plays an important role that keeps the gel in shape due to coupling of any change in different directions. This model predicts that the geometry of the gel is an important factor, and swelling is not a pure diffusion process.

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Several experimental techniques have been employed to study the kinetics of swelling, shrinking and drying of chemical and physical gels, e.g., neutron scattering [13], quasielastic light-scattering [12], macroscopic experiments [14] and in situ interferometric measurements. Using the fluorescence technique, a pyrene derivative was employed as a fluorescence probe to monitor the polymerization, aging and drying of aluminosilicate gels [15], where peak ratios in emission spectra were monitored during these processes. The volume phase transitions of poly (acrylamide) gels were monitored by fluorescence anisotropy and lifetime measurements of dansly groups [16]. Steady-state fluorescence (SSF) measurements on swelling of bulk gels formed by FCC of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDM) have been reported, where pyrene (Py) was used as a fluorescence probe to monitor swelling, desorption and drying processes in real time during in situ and time resolved fluorescence experiments [17–20].

In this work, we studied swelling process of PAAm hydrogels at various temperatures by using steady-state fluorescence technique. Li–Tanaka equation was used to determine the swelling time constants, τ_c and cooperative diffusion coefficients, D_c for the swelling processes. It was observed that swelling time constant, τ_c decreased and cooperative diffusion coefficients, D_c increased as the swelling temperature increased. The activation energies, ΔE were measured from fluorescence intensity, gravimetric and volume variations vs. temperature and found to be 10.7, 32.2 and 64.1 kJ mol^{-1}, respectively.

Theoretical considerations

It has been suggested [6] that the kinetics of swelling and shrinking of a polymer network or gel should obey the following relation

$$\frac{W_{(t)}}{W_{(\infty)}} = 1 - \sum_{n=1}^{\infty} B_n e^{\frac{-t}{\tau_n}} \tag{1}$$

where $W(t)$ and $W(\infty)$ are the swelling or solvent uptake at time t and at infinite equilibrium, respectively. $W(t)$ can also be considered as volume differences of the gel between the time t and zero. Each component of the displacement vector of a point in the network from its final equilibrium location after the gel is fully swollen, decays exponentially with a time constant τ_n, which is independent of time t. Here B_n is given by the following relation [6].

$$B_1 = \frac{2(3-4R)}{\alpha_1^2 - (4R-1)(3-4R)} \tag{2}$$

Here R is defined as the ratio of the shear and the longitudinal osmotic modulus, $R = G/M$. The longitudinal osmotic modulus, M is a combination of shear, G and osmotic bulk moduli, K, $M = K + 4G/3$, and α_n is given as a function of R as follows

$$R = \frac{1}{4}\left[1 + \frac{\alpha_1 J_0(\alpha_1)}{J_1(\alpha_1)}\right] \tag{3}$$

Here J_0 and J_1 are the Bessel functions.

In Eq. 1, τ_n is inversely proportional to the collective cooperative diffusion coefficient D_c of a gel disk at the surface and given by the relation [6]

$$\tau_n = \frac{3a^2}{D_c \alpha_1^2} \tag{4}$$

Here the diffusion coefficient D_c is given by $D_c = M/f = (K + 4G/3)/f$, f is the friction coefficient describing the viscous interaction between the polymer and the solvent, and a represent half of the disc thickness in the final infinite equilibrium which can be experimentally determined.

The series given by Eq. 1 is convergent. The first term of the series expansion is dominant at large t, which correspond to the last stage of the swelling. As it is seen from Eq. 4 τ_n is inversely proportional to the squared of α_n, where α_n's are the roots of the Bessel functionals. If $n > 1$, α_n increases and τ_n decreases very rapidly. Therefore kinetics of swelling in the limit of large t or if τ_1 is much larger than the rest of τ_n [21] all high-order terms ($n \geq 2$) in Eq. 1 can be dropped so that the swelling and shrinking can be represented by the first order kinetics [2]. In this case Eq. 1 can be written as

$$\frac{W(t)}{W_\infty} = 1 - B_1 e^{-t/\tau_c} \tag{5}$$

Equation 5 allows us to determine the parameters B_1 and τ_c.

Here it is important to note that Eq. 5 satisfies the following equation

$$\frac{dW(t)}{dt} = \frac{1}{\tau_c}(W_\infty - W) \tag{6}$$

which suggest that the process of swelling should obey the first order kinetics. The higher order terms ($n \geq 2$) can be considered as fast decaying perturbative additions to the first order kinetics of the swelling in the limit of large t.

Table 1 Experimentally measured parameters of PAAm hydrogels during swelling process

T (°C)	$a_i \times 10^{-2}$ (m)	$a_f \times 10^{-2}$ (m)	$r_i \times 10^{-2}$ (m)	$r_f \times 10^{-2}$ (m)	$V_i \times 10^{-7}$ (m^3)	$V_f \times 10^{-7}$ (m^3)	τ_{cI} (min)	$D_{cI} \times 10^{-9}$ (m^2 s^{-1})	τ_{cw} (min)	$D_{cw} \times 10^{-9}$ (m^2 s^{-1})	τ_{cv} (min)	$D_{cv} \times 10^{-9}$ ($m^2 s^{-1}$)
40	0.11	0.15	0.6	0.9	1.24	3.81	48.5	6	73	0.5	189	0.1
50	0.11	0.16	0.6	1.0	1.24	5.02	37.7	7.1	58	0.6	70	0.4
60	0.11	0.16	0.6	1.0	1.24	5.02	25	7.3	47	1.2	47	0.9
70	0.1	0.15	0.6	0.9	1.13	3.81	8	8.7	20	1.3	26	1.1

a_i, half of the disc thickness in the initial infinite equilibrium; a_f, half of the disc thickness in the final infinite equilibrium; r_i, radius of the disc in the initial infinite equilibrium; r_f, radius of the disc in the final infinite equilibrium; V_i, volume of the disc in the initial infinite equilibrium; V_f, volume of the disc in the final infinite equilibrium; τ_{cI}, time constant (fluorescence); τ_{cw}, time constant(gravimetric); τ_{cv}, time constant (volumetric); D_{cI}, cooperative diffusion coefficient (fluorescence); D_{cw}, cooperative diffusion coefficient (gravimetric); D_{cv}, cooperative diffusion coefficient (volumetric)

Materials and methods

Gels were prepared by using 2M AAm (Merck) and BIS (Merck) by dissolving in 25×10^{-6} m^3 of water in which 10×10^{-9} m^3 of TEMED (tetramethylethylenediamine) were added as an accelerator. The initiator, ammonium persulfate (APS, Merck), was recrystallized twice from methanol. The initiator and pyranine concentrations were kept constant at 7×10^{-3} and 4×10^{-4} M, respectively, for all experiments. All samples were deoxygenated by bubbling nitrogen for 10 min, just before polymerization process [21].

The swelling experiments of disc shape PAAm gels were performed at various temperatures. Details of the samples are listed in Table 1 (a_i, a_f, r_i, r_f, V_i, and V_f are half thickness, radius and volume of diskshape gels).

The fluorescence intensity measurements were carried out using the Model LS-50 spectrometer of Perkin–Elmer, equipped with temperature controller. All measurements were made at 90^ position and slit widths were kept at 5 nm. Pyranines in the PAAm hydrogels were excited at 340 nm during in situ experiments and emission intensities of the pyranine were monitored at 427 nm as a function of swelling time. A disc-shaped gel samples were placed on the wall of 1×1 quartz cell filled with water for the swelling experiments. The position of the gel and the incident light beam for the fluorescence measurements are shown in Fig. 1 during swelling in water. Here one side of the quartz cell is covered by black cartoon with a circular hole to collimate the light beam so that minimize the effect of changes in the volume.

Gravimetric and volumetric experiments were performed at the same condition as fluorescence experiments were done. Measurements were made by microbalance and a micrometer, respectively. We prepared two samples for each gel. One of them was placed in the spectrometer sample holder for the fluorescence measurements. At the same time, the other one was used for the gravimetric and the volumetric measurements.

Results and discussion

The fluorescence spectra of the fluorescence molecule pyranine are shown in Fig. 2. Pyranine has two distinct spectra in sol and gel states, respectively. It is seen from the Fig. 2 that the emission wavelength is 512 nm in the sol state where pyranine dissolved in pure water. During the polymerization the emission wavelength shifts from 512 to 427 nm due to binding of pyranine molecules to the polymer [23]. It is seen from the Fig. 2 that the emission wavelength is 427 nm in the gel state. Figure 3 shows the emission spectra of pyranine in PAAm gel during the swelling process in pure water. It can be seen that as the water uptake is increased fluorescence intensity, I_{em} decreases and the scattered light intensity, I_{sc} increases. Since the increase in I_{sc} corresponds to increase in turbidity of the swelling gel, then we have defined corrected fluorescence intensity, I as I_{em}/I_{sc}. The variations of corrected pyranine intensities, I vs. swelling time during hydrogel swelling at various temperatures are presented in Fig. 4. It can be seen that as the swelling time, t, is increased, quenching of excited pyranines increase due to water uptake. It has also to be noted that quenching be comes more efficient at higher temperatures. In order to quantify these results the collisional type of quenching mechanism may be proposed for the fluorescence intensity, I in the gel sample during swelling process, where the following relations are given [22]

$$I^{-1} = I_0^{-1} + k_q \tau_0 [Q] \tag{7}$$

Here, k_q is quenching rate constant, τ_0 is the lifetime of fluorescence probe and Q is the quencher.

For low quenching efficiency, $(\tau_0 k_q [Q] \ll 1)$, Eq. 7 becomes

$$I \approx I_0 (1 - k_q \tau_0 [Q]) \tag{8}$$

If one integrates Eq. 8 over the differential volume (dv) of the gel from the initial, a_0 to final a_∞ thickness and then,

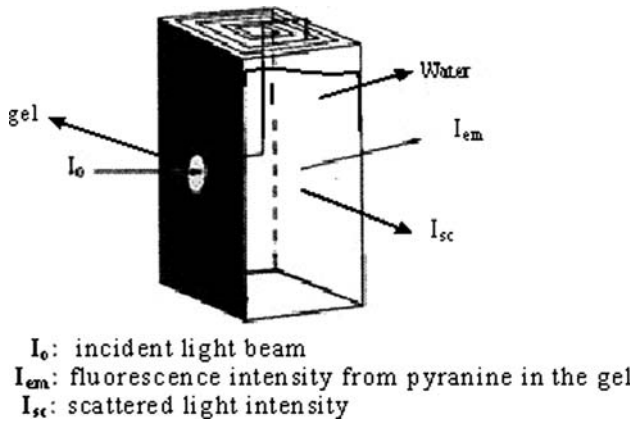

Fig. 1 The position of PAAm hydrogel in the fluorescence cell during swelling in water. I_0 is excitation, I_{em} is emission and I_{sc} is scattered light intensities at 340 and 427 nm, respectively

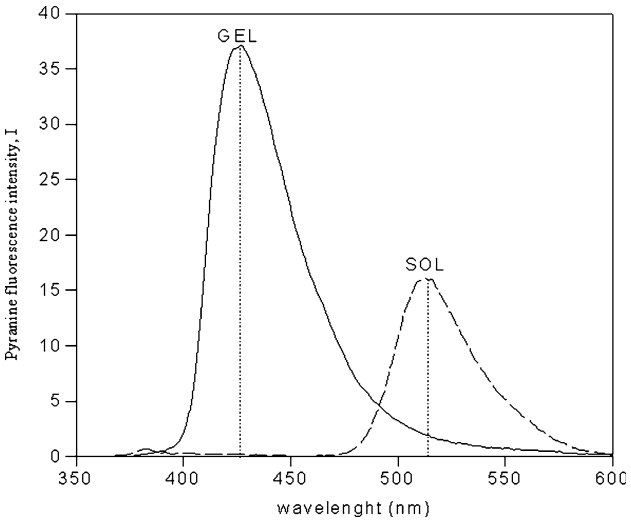

Fig. 2 Fluorescence spectra of pyranine molecule, in gel and sol states, respectively

reorganization of the relation produces the following useful equation.

$$W = \left(1 - \frac{I}{I_0}\right)\frac{\upsilon}{k_q \tau_0} \tag{9}$$

Here water uptake, W is calculated over differential volume by replacing Q with W as

$$W = \int_{a_0}^{a_\infty} [W] \mathrm{d}\upsilon \tag{10}$$

where υ is the swollen volume of the gel at the equilibrium swelling, which can be measured experimentally. k_q was obtained from separate measurements by using Eq. 9

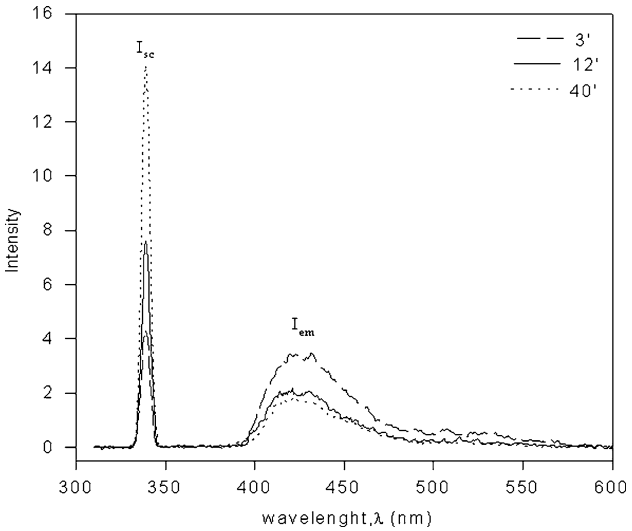

Fig. 3 Fluorescence spectra of Pyranine during the swelling process. The numbers indicate the swelling times

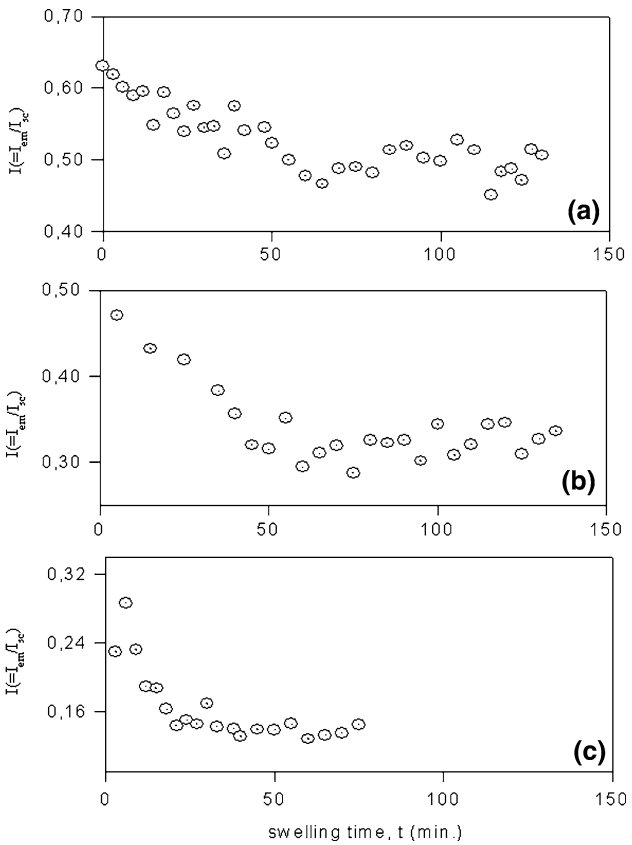

Fig. 4 Corrected fluorescence intensities of pyranine, I (= I_{em}/I_{sc}) during the swelling process at (**a**) 40, (**b**) 60 and (**c**) 70 °C temperatures

where the infinity equilibrium value of water uptake, W_∞ was used at each temperature. Since τ_0 ($\approx$ 5ns.) is already known from the dry gel, and measured values of υ can be

used to calculate k_q at each temperature separately. The average value of k_q is found around 0.39×10^7 M^{-1} s^{-1}. Once k_q values are measured, the water uptakes, W can be calculated from the measured τ values at each swelling step. Here, it is assumed that k_q values do not vary during swelling processes, i.e., the quenching process solely originates from the water molecules.

Plots of water uptake, $W(t)$ vs. swelling time are presented in Fig. 5. The logarithmic form of the data in Fig. 5 are fitted to the following relation produce from Eq. 5

$$\ln\left(1-\frac{W}{W_\infty}\right) = \ln B_1 - \frac{t}{\tau_{cI}} \tag{11}$$

Using Eq. 11 linear regressions of curves in Fig. 6 provide us with B_1 and τ_{cI} values. Taking into account the dependence of B_1 on R, one obtains R values and from α_1–R dependence α_1 values were produced [6]. Then using Eq. 4, cooperative diffusion coefficients D_c were determined for these disc-shaped hydrogels and found to be around 10^{-9} m^2/s. Experimentally obtained τ_{cI} and D_{cI} values are summarized in Table 1, where a, and r (radius) values are also presented for each gel.

The plots of the solvent uptake, W, vs. swelling time measured by gravimetrically for hydrogels, swollen in water are shown in Fig. 7. These are typical solvent uptake curves, obeying the Li–Tanaka equation Eq. 5. The logarithmic forms of the data in Fig. 7 are fitted to the following relation produced from Eq. 5.

$$\ln\left(1-\frac{W}{W_\infty}\right) = \ln B_1 - \frac{t}{\tau_{cw}} \tag{12}$$

The fits are presented in Fig. 8, from which B_1 and gravimetric time constant, τ_{cw} are produced. Then using Eq. 4 gravimetric cooperative diffusion coefficients D_{cw} were determined and are listed in Table 1 with τ_{cw} values.

The variations in volume, v of PAAm hydrogels during the swelling process are also measured at the same condition of fluorescence experiments. The plots of the volume, v, vs. swelling time for PAAm hydrogels swollen in water are presented in Fig. 9, which are again typical solvent uptake curves, obeying the Li–Tanaka equation Eq. 5. The logarithmic forms of the data in Fig. 9 are fitted to the following relation produced from Eq. 5.

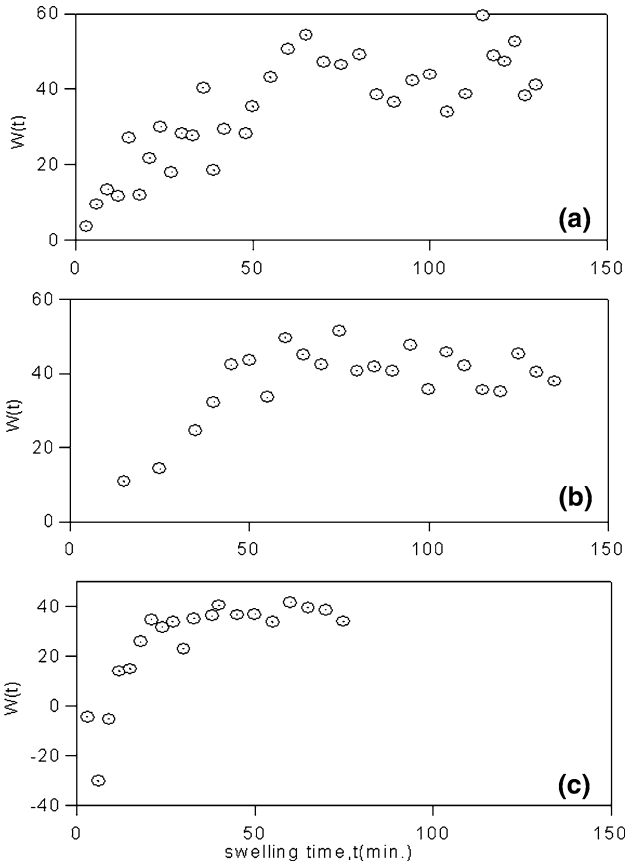

Fig. 5 The plots of water uptake, $W(t)$ vs. swelling time, t for PAAm hydrogels swollen in water at (**a**) 40, (**b**) 60 and (**c**) 70 °C temperatures

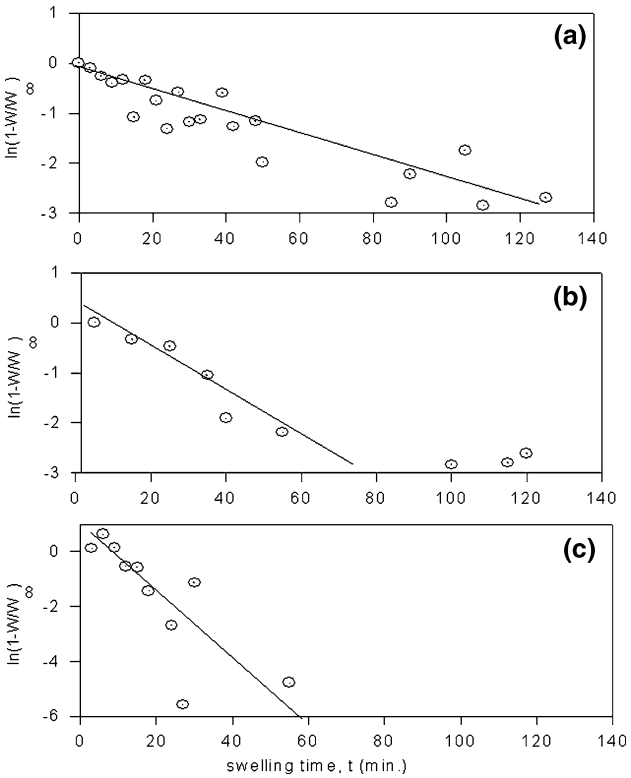

Fig. 6 Fit of the data in Fig. 4 to Eq. 5 for PAAm hydrogels swollen in water at (**a**) 40, (**b**) 60 and (**c**) 70 °C temperatures

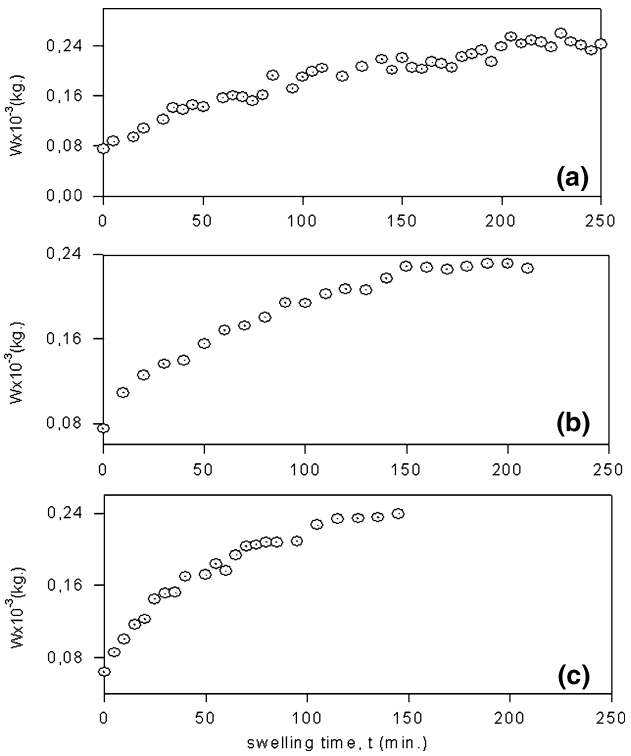

Fig. 7 The plots of the water uptake, W measured by gravimetrically, vs. swelling time, t, for PAAm hydrogels swollen in water at (**a**) 40, (**b**) 50, and (**c**) 60 °C temperatures

$$\ln\left(1-\frac{v}{v_\infty}\right)=\ln B_1-\frac{t}{\tau_{cv}} \tag{13}$$

Here it is assumed, that the relation between W and v are linear. The fits are presented in Fig. 10, from which B_1 and

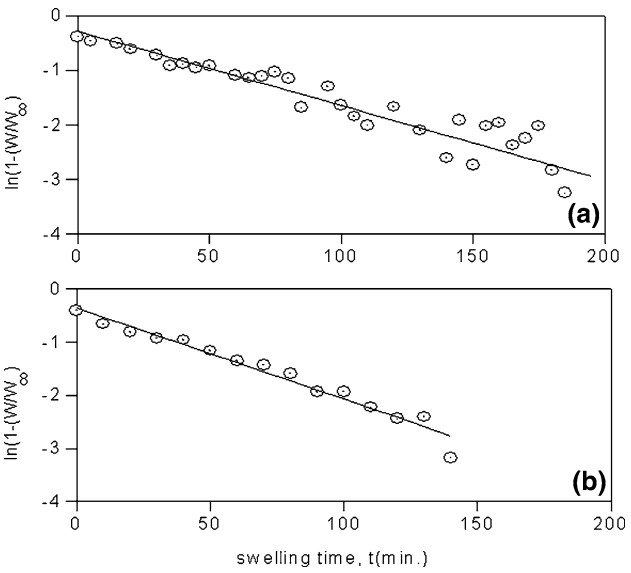

Fig. 8 Linear regressions of the data in Fig. 6 according to Eq. 12 for PAAm hydrogels swollen in water at (**a**) 40 and (**b**) 50 °C temperatures

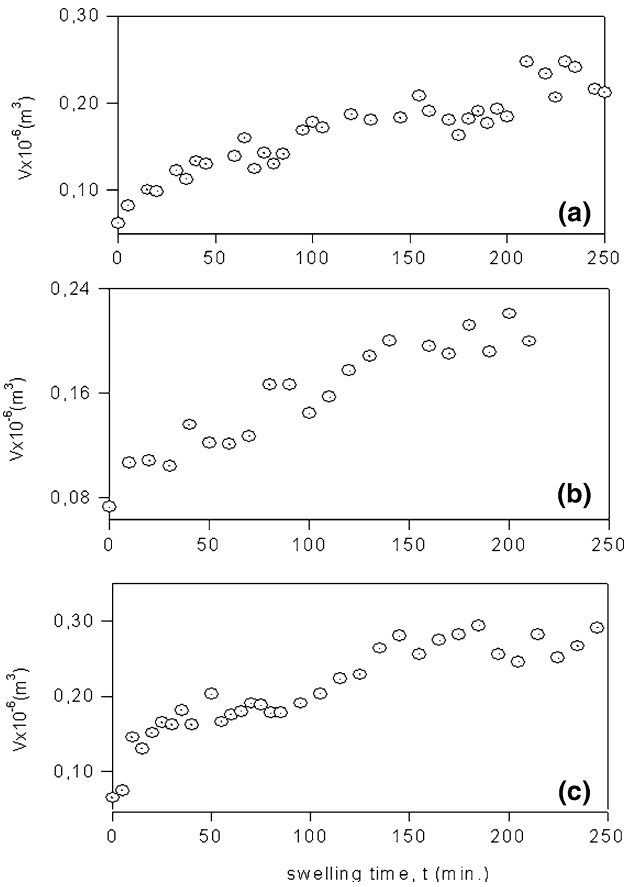

Fig. 9 The plots of changing in the volume, v, vs. swelling time, t, for PAAm hydrogels swollen in water at (**a**) 40, (**b**) 50 and (**c**) 60 °C temperatures

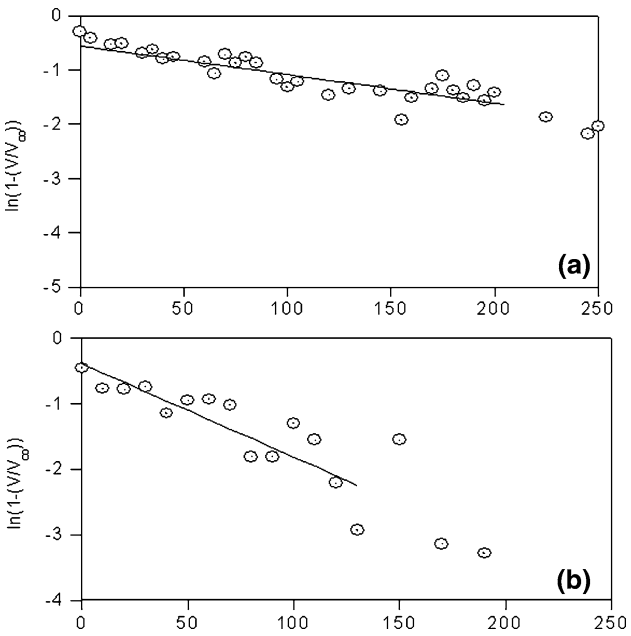

Fig. 10 Linear regressions of the data in Fig. 8 according to Eq. 13 for PAAm hydrogels swollen in water at (**a**) 40 and (**b**) 50 °C temperatures

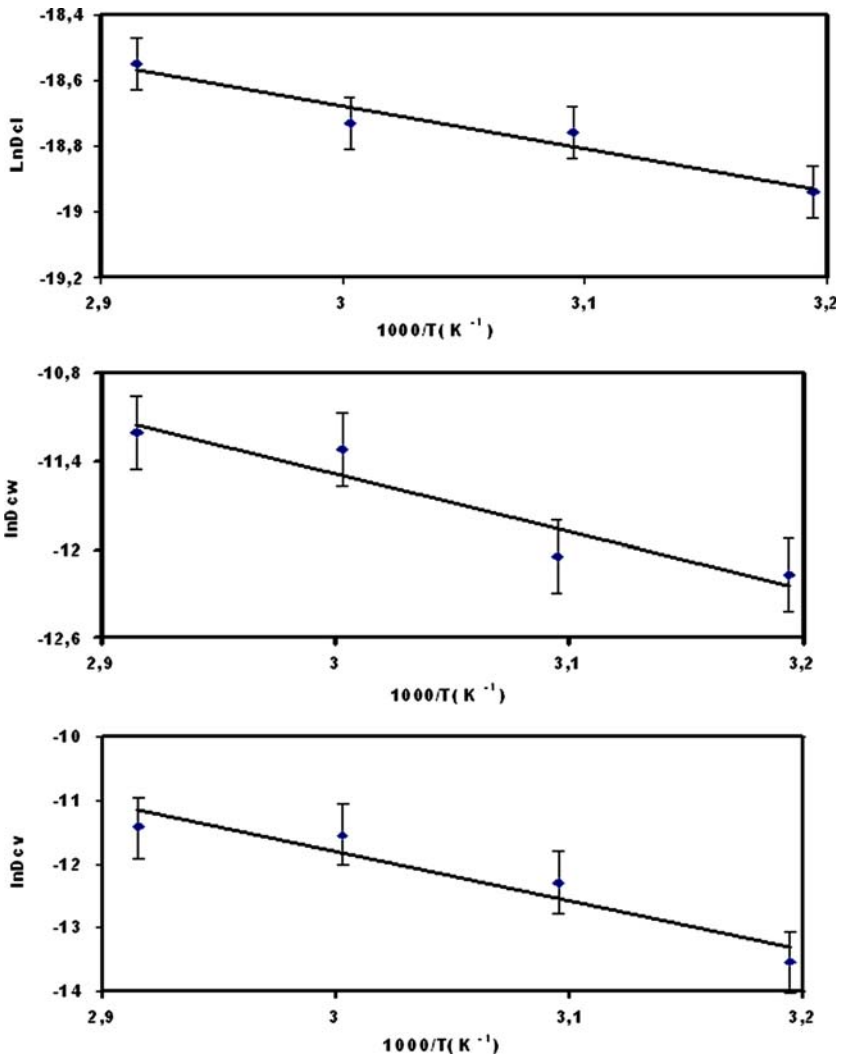

Fig. 11 The logarithmic plots of D_c values vs. inverse temperature T^{-1} according to Eq. 14. The slopes of the linear relation produce the activation energies, ΔE for the swelling process

τ_{cv}, volumetric time constant, values are produced. Then using Eq. 13 volumetric cooperative diffusion coefficients D_{cv} were determined and listed in Table 1 with τ_{cv} values. Here it is seen in Table 1 that D_c values measured by using fluorescence technique are at least order of magnitude much larger than the values measured by volumetric and gravimetric techniques, which may present the different behaviors of the gel. It is obvious that the fluorescence technique measure the behavior of the microstructure of the gel, i.e., segmental motion of the gel network can be monitored by using fluorescence intensity, because pyranine molecules are bounded to the polymer chains. However, volumetric and gravimetric measurements may provide us with the information of the macroscopic behavior (i.e., bulk environment). According to the above argument, one may suggest that chain segments move much faster than the bulk polymeric material during swelling process.

On the other hand, D_c–T relations in Table 1 may be treated by the following Arrhenius law.

$$D_c = D_{co} \cdot \exp(-\Delta E/kT) \tag{14}$$

where the ΔE is the activation energy for swelling, k is the Boltzmann's constant and D_{co} is the cooperative diffusion coefficient at $T = \infty$. The logarithmic form of the D_{cI}, D_{cw} and D_{cv} values, found from fluorescence intensity, gravimetric and volumetric techniques, are plotted vs. T^{-1} in Fig. 11 where the slopes of the linear relations produced the activation energies ΔE_I, ΔE_w and ΔE_v for the swelling gel as 10.7, 32.2 and 64.1 kJ mol^{-1}, respectively. Once again, one can see that the energy need for segmental motion is much lower than the bulk motion of the swollen gel samples. In other words activation energy measured by fluorescence technique monitors the gel behavior at the molecular level, however gravimetric and volumetric techniques measures the bulk behavior of the gel. On the other hand, when the activation energy produced from the fluorescence technique is compared with our previous finding [23], where polystyrene (PS) gel was swollen in chloroform vapor. The observed value (80 kJ mol^{-1}) was

found to be eight times larger than that our recent observation. Here one may argue that penetration of water molecules into PAAm hydrogel needs much less energy than chloroform molecules penetrating into PS gel. Most probably, elastic forces in PS gel network oppose the penetrating chloroform molecules stronger than they do in PAAm hydrogel, which may have less resistance against water molecules.

Conclusion

These results have shown that the direct fluorescence method can be used for real-time monitoring of hydrogel swelling process. Li–Tanaka equation was used to determine the swelling time constants, τ_c and cooperative diffusion coefficients, D_c for the swelling processes. In this method in situ fluorescence experiments are easy to perform and provide us with quite sensitive results to measure the swelling parameters in water environment.

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