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In situ Fluorescence Study of Swelling, Sorption and Desorption Processes in and out of PAAm Gels

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Summary: Small molecule sorption and desorption in and out of polyacrylamide (PAAm) gels were studied at various temperatures. Pyranine (P_y) dissolved in water used as a probe. Fluorescence emission intensity, I_p from P_y was monitored for studying sorption and desorption processes. Scattered light intensities, I_{sc} from PAAm gel was also monitored to observed structural variations during sorption and desorption process. Li-Tanaka model was applied to produce the swelling time constants, τ_c and sorption coefficients, D_c for the swelling processes. On the other hand, sorption and desorption processes were studied and coefficients were produced by using Fickian model. Related activation energies were also calculated from the corresponding physical processes.

Keywords: desorption; fluorescence; hydrogels; sorption; temperature

Introduction

The sorption, swelling and desorption kinetics of physical and chemical gels are very important in various fields of industry: in the pharmaceutical industry in designing desorption devices for drugs, in the agricultural industry for producing storable foods, and in medical industry in developing artificial organs.

The imperfections in the hydrogel structures have been known to influence the solvent permeability, the sorption of small and large molecules and more indirectly the swelling properties of gels. In the swollen state these imperfections manifest themselves in a nonuniformity of polymer concentration. Considerable work has been done on the characterization of the gel inhomogeneities. It was shown that high permeability of polyacrlamide (PAAm) gels is related to the inhomogeneous cross-link distribution.[1] The effect of inhomogeneities of the polymer network on the swollen state of acrylamide gels and on the diffusion of water molecules within the gels were examined.[2] When an ionized acrylamide gel is allowed to swell in water, an extremely interesting pattern appears on the surface of the gel and the volume expansion increases by adding some amount of sodium acrylate.[3] If acrylamide gels are swollen in acetone-water mixture, gel aging time plays an important role during collapse of the network.[4] The kinetics of swelling of acrylamide gels was studied by light scattering and the cooperative diffusion coefficient of the network was measured.[5,6] Small angle x-ray and dynamic light scattering were used to study the swelling properties and mechanical behavior of acrylamide gels.[7]

The swelling process of chemically cross-linked gels can be understood by considering the osmotic pressure versus the restraining force.[8–12] Two polymeric hydrogels containing (PVP) - crosslinked polyacrylamide and poly (vinyl alcohol) (PVA)-crosslinked polyacrylamide were loaded with the sulfamethoxazole drug and their swelling and drug-release dynamics were investigated at a fixed pH and at room temperature (27 °C).[13] Swelling, deswelling and drug release properties were studied on polyDEAAm-based and

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polyNIPAAm hydrogels.[14] The use of hydrophobically modified hydrogels for drug release was examined.[15] Swelling and controlled- release behaviors of hydrophobically modified poly (methacrylic acid) hydrogels were investigated.[16]

Photon transmision technique was used to study gelation and swelling process of PAAm where transmitted light intensity decreased and increased during gel formation and swelling processes respectively.[17–19] Similar technique was employed to study N-isopropylacrylamide gels.[20,21] On the other hand, time resolved and steady state (SSF) fluorescence techniques were employed for studying swelling and diffusion processes in PMMA gels.[22,23] Steady state (SFF) fluorescence techniques were employed for studying slow release in various solvents.[24] By using the same method, small molecule diffusion into hydrogels at various temperatures was obtained in our laboratory.[25]

In this work, sorption, swelling and desorption kinetics of PAAm at various temperatures was studied by using steady-state fluorescence (SSF) technique. Pyranine (P_y) dissolved in water was used as fluorescence probe to study sorption and desorption process. Pyranine emission intensity, I_p was monitored to investigate these processes at various temperatures. Scattered light intensities, I_{sc} from PAAm gel was elaborated for studying swelling processes. Li-Tanaka model was used to determine the swelling time constants, τ_c and cooperative sorption coefficients, D_{sc} for the swelling gels. Fickian model was employed to produce sorption and desorption coefficients. The corresponding activation energies were also obtained.

Theoretical Considerations

Kinetics of Swelling

Swelling experiments of disc shaped gels have shown that the relative changes of diameter and thickness are the same, indicating that the gel-swelling processes are not pure diffusional processes. In fact the equality of the relative changes of diameter thickness stems from the none zero shear modulus, μ which results; the change of the total shear energy in response to any small change in shape that maintains constant volume element within the gel should be zero. The high friction coefficient, f between the network and the solvent overdamps the motion of the network, resulting in diffusion like relaxation. The equation of the motion of a network element during the swelling can be given by[8]

$$\frac{\partial \vec{u}}{\partial t} = D_C \vec{\nabla}^2 \vec{u} \qquad (1)$$

where $\vec{u}$ is the displacement vector measured from the final equilibrium location after the gel is fully swollen ($u = 0$ at $t = \infty$). $D_c = (K + 4\ \mu/3)/f$ is the collective diffusion coefficient. Here t denotes the time and K is the bulk modulus. Equation (1) has been used with some success to study the swelling of gels.[22] However, these studies did not properly treat the shear deformation that occurs within a gel during swelling, and, hence, can not explain, for example, the isotropic swelling of a cylindrical gel. This shortcoming was due to the shear modulus of the network keeping the system in shape by minimizing the non-isotropic deformation. For a disc shaped gel, any change in diameter is coupled to a change in thickness. The total energy of a gel can be separated into bulk energy and shear energy. The bulk energy is related to the volume change, which is controlled by sorption. The shear energy, F_{sh} on the other hand, can be minimized instally by readjusting the shape of the gel[8]

$$\delta F_{sh} = 0 \qquad (2)$$

Simultaneous solution of Equation (1) and (2) produces the following equation for the swelling of a gel disc in terms of vapor and solvent uptakes W and W_∞ at time t and at equilibrium respectively as follows

$$\frac{W_\infty - W}{W_\infty} = \sum_{n=1}^{\infty} B_n \exp(-t/\tau_n) \qquad (3)$$

In the limit of large t, or if τ_c is much larger than the rest of τ_n, all higher terms ($n \geq 2$) in Equation (3) can be omitted and the swelling kinetics is given by the following relation

$$\left(1 - \frac{W}{W_\infty}\right) = B_1 \exp(-t_s/\tau_c) \tag{4}$$

It should be noted from Equation (3) that $\Sigma B_n = 1$, therefore B_1 should be less than 1. B_1 is related to the ratio of the shear modulus, μ and longitudinal osmotic modulus, $M = (K + 4\,\mu/3)$. Hence, once the value of B_1 is obtained, one can determine the value of $R = \mu/M$. Here we have to note that Equation (4) can also be obtained by using the theoretical results,[5] in the case of $R \rightarrow 3/4$ ($\mu/K \rightarrow \infty$), time constant $\tau_c \approx (3/4 - R)^{-1}$ goes to infinity and all B_n's go to zero except B_1, which goes to unity. The dependence of B_1 on R for a disc can be found in the literature.[22] τ_c is related to the collective diffusion coefficient D_c at the surface of a gel disc by

$$D_c = \frac{3a^2}{\tau_c \alpha_1^2} \tag{5}$$

where α_1 is a function R only and is given the literature,[5] and a stands for the half thickness of the gel in the final equilibrium state. Hence, D_c can be calculated, if one obtains τ_c values from the swelling experiments.

Fickian Model

According to Fick's law, the equation for diffusion in one dimension, when the diffusion coefficient D is constant, is expressed[26,27] as

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) = D\frac{\partial^2 c}{\partial x^2} \tag{6}$$

where c is the concentration of diffusing species at time, t. For a plane sheet geometry and keeping constant the initial concentration of water, the solution of the Fick equation is given by the equation

$$\frac{M}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left(\frac{-D(2n+1)^2\pi^2 t}{d^2}\right) \tag{7}$$

where d is the thickness of the specimen and M and M_∞ are the masses of water sorbed or desorbed at times t and ∞, respectively.

Experimental Part

Each gel was prepared by using 0.71×10^{-3}kg AAm (Acrylamide) and 0.008×10^{-3}kg APS (Ammonium per sulfate) as an initiator by dissolving them in 5×10^{-3}l of water in which 0.5 μl of TEMED(tetramethylethylenediamine) was added as an accelerator. 0.01×10^{-3}kg BIS (N′-methylenebis (acrylamide)) was used as a crosslinking agent. This stock solution was deoxygenated by bubbling nitrogen through it for 10 min just before the polymerization process. It was transferred into round glass tubes of 0.99×10^{-2}m internal diameter. Pyranine concentration was kept at 10^{-4}M for all samples. Free radical crosslinking copolymerization (FCC) was performed (for each sample) at room temperature.

Perkin Elmer LS 50 spectrophotometer equipped with temperature controller was used for fluorescence studies. All measurements were made at the 90° position and slit widths were kept at 5 nm. 340 nm was chosen for excitation light and emission was detected at 512 nm during sorption, swelling and desorption experiments. Cell positions are presented in (Figure 1a and b), during sorption and desorption experiments respectively. Sorption and swelling experiments were designed by placing pyranine solution in water, on top of the gel at room temperature. Incident light, I_0 was directed into the gel to monitor sorption of pyranine molecules into PAAm gel. Scattered light intensities, I_{sc} from PAAm gel was also monitored to observed structural variations during sorption which corresponds to swelling process. After the sorption process is completed i.e. gel was

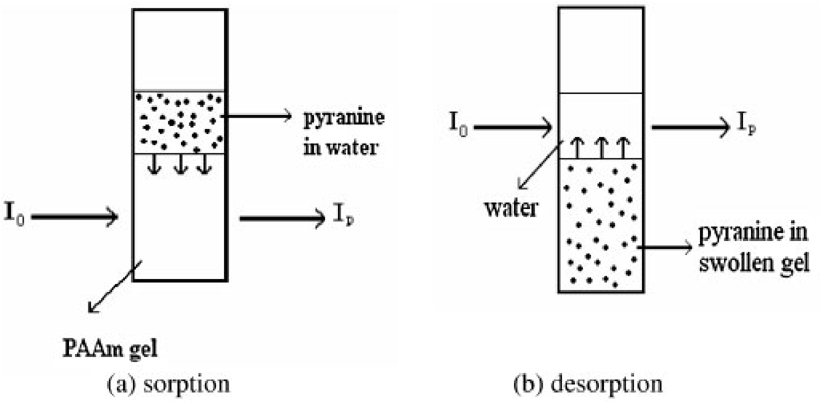

Figure 1.
Position of the gel during a-sorption, b- desorption.

saturated by pyranine molecules, pure water was then placed on top of the pyranine saturated gel to monitor desorption process. This time incident intensity is directed to water to detect the releasing pyranine molecules out of the gel.

Results and Discussion

Scattering intensity, I_{sc} versus swelling time, t is plotted in (Figure 2) for the gels swell at various temperatures. The numbers in (Figure 2) correspond to temperatures in °C. It is seen in (Figure 2) that, I_{sc} decrease by increasing swelling time, indicating that lattice heterogeneities disappear during water uptake of the gel under consideration. It should be noted that water uptake is much faster in gels at high temperatures. These results can be quantified by assuming that the water uptake, W is proportional to the transmitted light intensity, $I_{tr} = 1 - I_{sc}$. During swelling, as more water molecules enter into the gel, structural heterogeneities are disappeared as a result I_{sc} decreases as W increases.

(Figure 3) presents the results of the sorption experiments where P_y intensity, I_p increases as sorption time increased for the all gel samples. Here numbers represent the temperatures. Since I_p is directly proportional to the number of P_y molecules enter into the gel, the behavior of the intensity

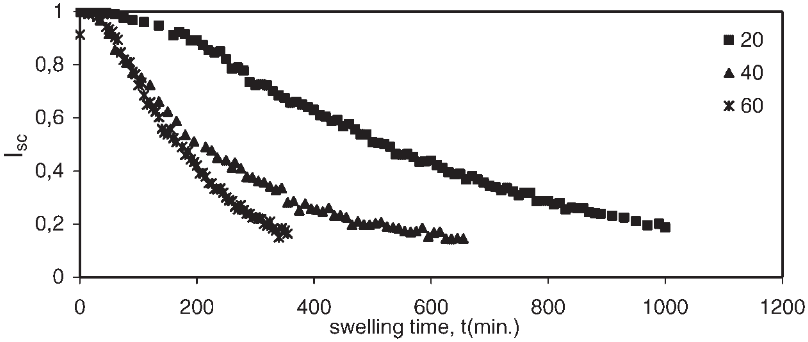

Figure 2.
Scattered light intensity, I_{sc} curves against swelling time, t, for the gels kept at 20 °C, 40 °C, and 60 °C temperatures.

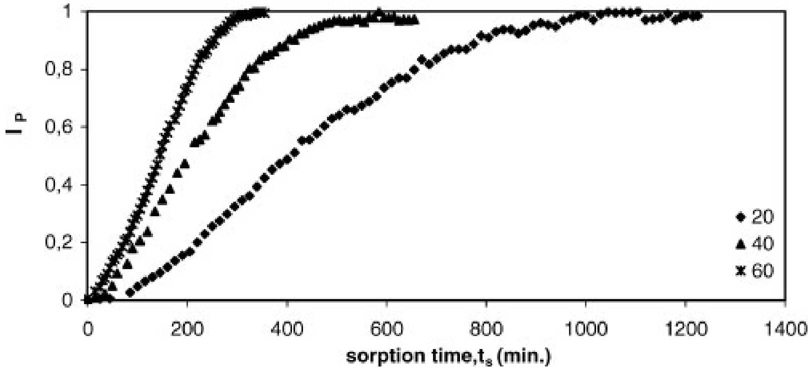

Figure 3.

The behavior of P_y intensity, I_p versus time of P_y sorption in of PAAm gels, kept at 20, 40, and 60 °C temperatures.

curves in (Figure 3) suggest that P_y molecules are absorbed much faster at higher temperatures.

Under this picture the sorption process can be treated using the Fickian diffusion model. The plot of I_p versus desorption time t_{sl} for desorption processes are plotted in (Figure 4). Desorption curves in (Figure 4) present continuous increase, till they saturate.

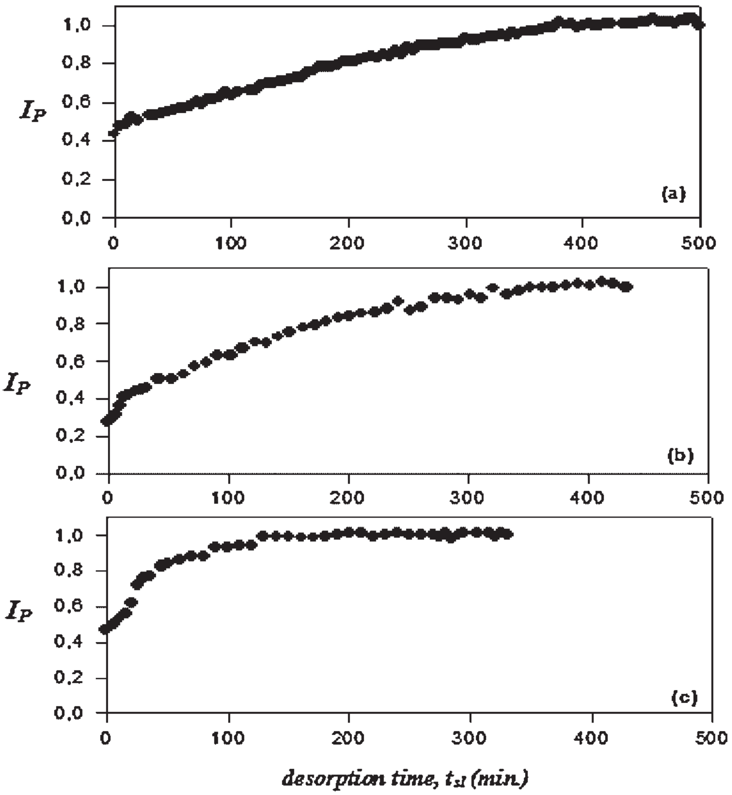

Figure 4.

Plot of P_y intensity, I_p during desorption at different temperatures a-20 °C, b-40 °C, and c-60 °C. $\mathbf{t_{sl}}$ represents the desorption time.

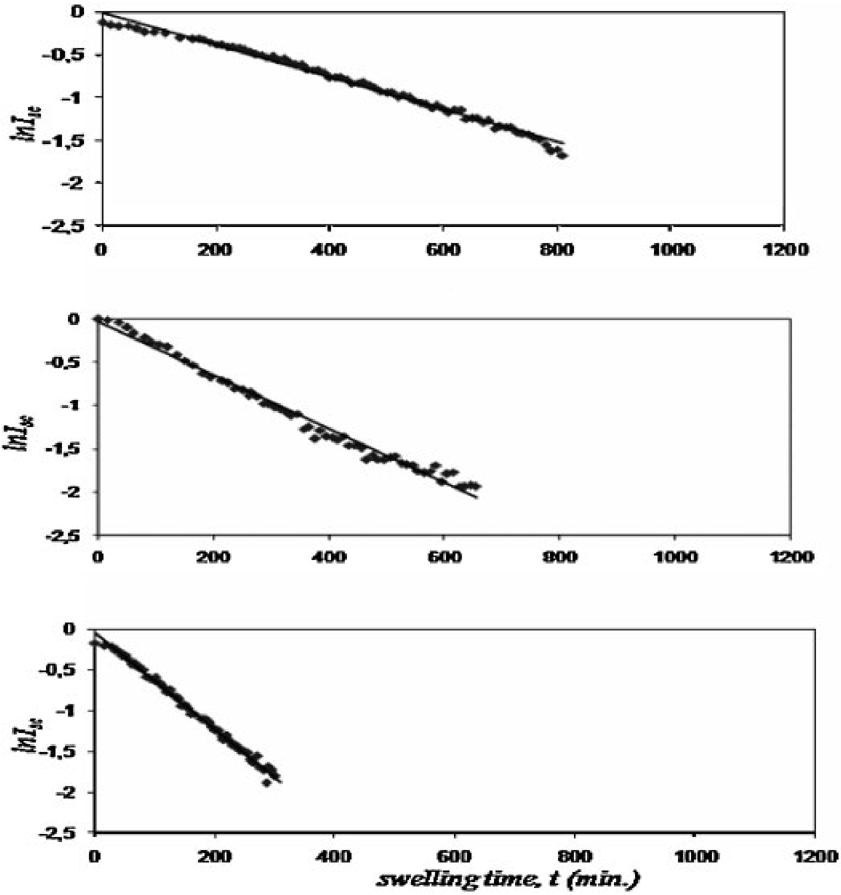

Figure 5.
Linear regression of the curves given in (Figure 2). The intercept and the slope of the curves produce B_1 and τ_c parameters.

In order to model the swelling processes, Equation (4) can be written in terms of I_{sc} in the logarithmic form, i.e.

$$\ln(I_{sc}) = \ln B_1 - t/\tau_c \qquad (8)$$

Linear regression of curves in (Figure 5 a, b and c), using Equation (8) provides us with B_1 and τ_c values as shown in (Figure 5). Taking into account the dependence of B_1 on R one obtains R values and from $\alpha_1 - R$ dependence, α_1, values were produced.[8] Then using Equation (5) cooperative diffusion coefficients, D_{sc} were determined for PAAm gels. Experimentally obtained parameters, τ_c and B_1 together with a and D_{sc} values are summarized in (Table 1) for various temperatures. Here one should have noticed that measured D_{sc} values present larger numbers at high temperature. This result is expected, since swelling

Table 1.
Experimentally produced swelling time constants, τ_c preexperimental factors, B_1, and collective sorption coefficients, D_{sc}. a is the half thickness of PAAm gels at the final equilibrium state.

T (°C)	τ_c (s)	B_1	$D_{sc} \times 10^{-8}$ (m^2s^{-1})	$a \times 10^{-2}$ (m)
20	526.31	0.98	0.864	0.51
30	434.78	0.98	0.905	0.55
40	322.50	0.97	0.918	0.56
50	285.71	0.96	1.045	0.62
60	169.49	0.94	1.378	0.625

process is much faster at higher temperatures.

In the sorption experiment, PAAm gels are assumed to be as thin slabs, then the logarithmic form of Equation (7) for $n = 0$ can be given as follows

$$\ln\left(1 - \frac{I_p}{I_{p_\infty}}\right) = \ln\left(\frac{8}{\pi^2}\right) - \frac{D\pi^2}{d^2}t \qquad (9)$$

The fit of the Equation (9) to the data in (Figure 3) are given in (Figure 6), from where D_s and D_l values are produced and are listed (Table 2). As expected, it is seen that D values for the gels at high temperature are much larger than they are at low temperature. Here it is seen in (Figure 6), that sorption of P_y molecules has two distinct regions, namely short and long times, produces two different sorption coefficients as D_s and D_l respectively.

Similarly desorption data in (Figure 4) are also treated in (Figure 7) by using Equation (9) and produced desorption coefficients, D_{sl} which are listed in (Table 3). Again, here D_{sl} values present

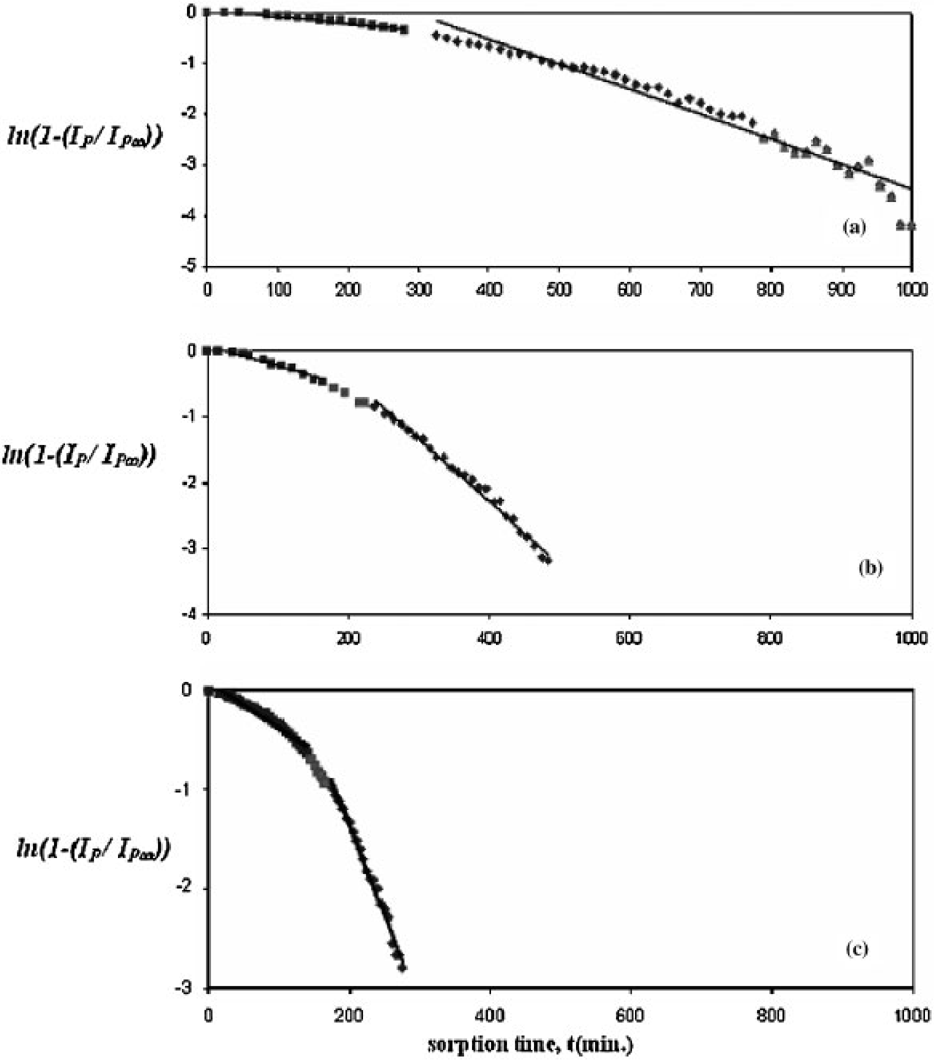

Figure 6.
Linear regression of the data in (Figure 3). The slopes of the straight lines produce D values.

Table 2.
Experimentally produced sorption coefficients, D_s and D_l. d is the thickness of PAAm gels at 20, 30, 40, 50 and 60 °C.

T (°C)	$D_{sc} \times 10^{-8}$ (m^2s^{-1})	$D_l \times 10^{-8}$ (m^2s^{-1})	$d \times 10^{-2}$ (m)
20	1.37	4.01	1.02
30	1.87	4.87	1.11
40	3.94	10.45	1.12
50	4.05	14.65	1.24
60	7.28	28.84	1.25

increase as the temperature is increased as expected. If one compares (Table 2) with (Table 3) it can be seen that desorption process is much slower than the two regions.

Table 3.
Experimentally produced desorption coefficients, D_{sl}. l is the initial thickness of the swollen PAAm gels at 20, 30, 40, 50 and 60 °C.

T (°C)	$D_{sl} \times 10^{-10}$ (m^2s^{-1})	$d \times 10^{-2}$ (m)
20	2.01	1.02
30	2.39	1.11
40	6.57	1.12
50	7.90	1.24
60	9.31	1.25

Arrhenius equation now can be used in all cases

$$D = D_0 e^{-\Delta E/kT} \tag{10}$$

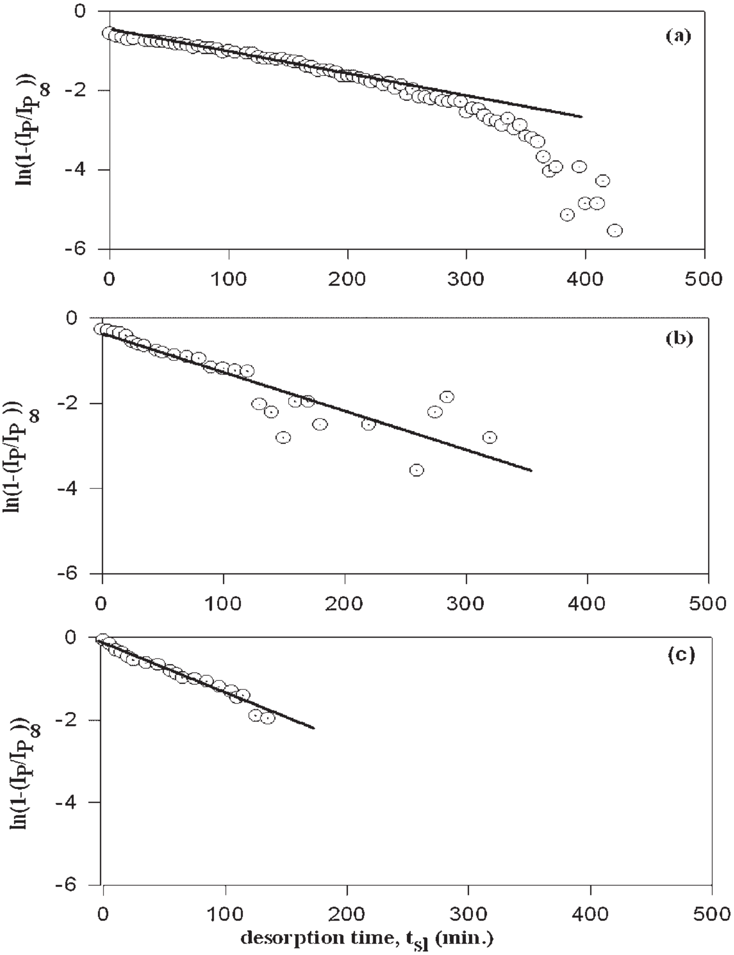

Figure 7.
Fits of the desorption data in (Figure 4). to Equation (9). The slope of the straight lines produce desorption coefficients, D_{sl} at a-20 °C, b-40 °C, c-60 °C.

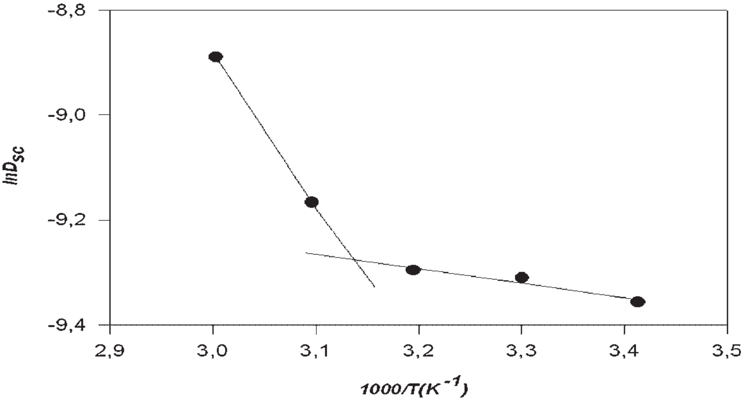

Figure 8.
Arrhenius treatment of D_{sc} values. The slopes of the straight line produce the two different activation energies, namely ΔE_1 and ΔE_2 for gel swelling.

to calculate activation energies, ΔE. (Figure 8) shows the Arrhenius treatment of D_{sc} from which the activation energies, ΔE_1 and ΔE_2 at low and high temperature regions for gel swelling are calculated, and found to be 24,69 kJmol^{-1} and 2.29 kJmol^{-1} respectively.

These values of activation energies are much smaller than the produced activation energy for PMMA in chloroform in the same temperature region.[22] From here one may conclude that the energy need for hydrogel swelling is very small compared to the organic solvent base systems. This

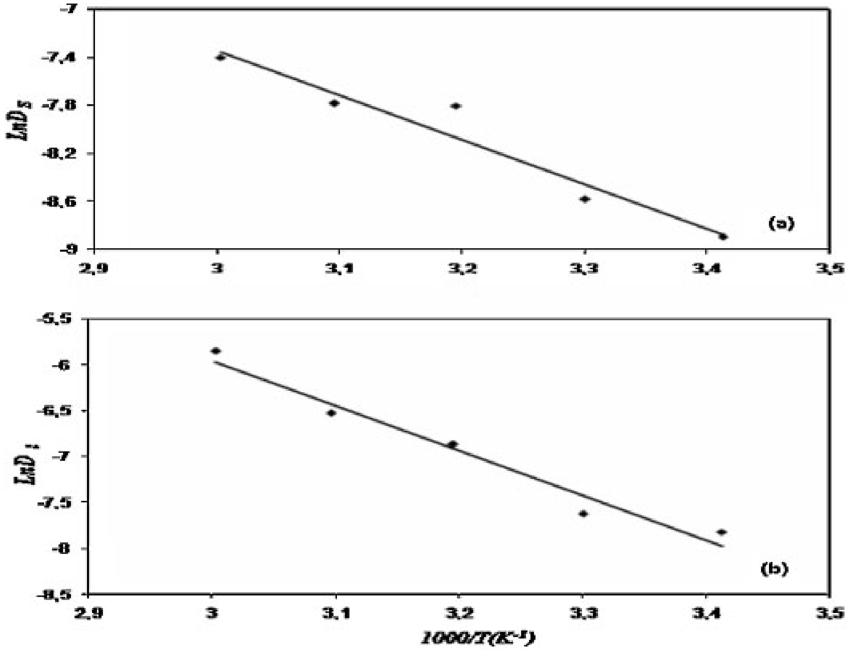

Figure 9.
Arrhenius treatment of a- short b-long time sorption coefficients which produced ΔE_s and ΔE_l activation energies, respectively.

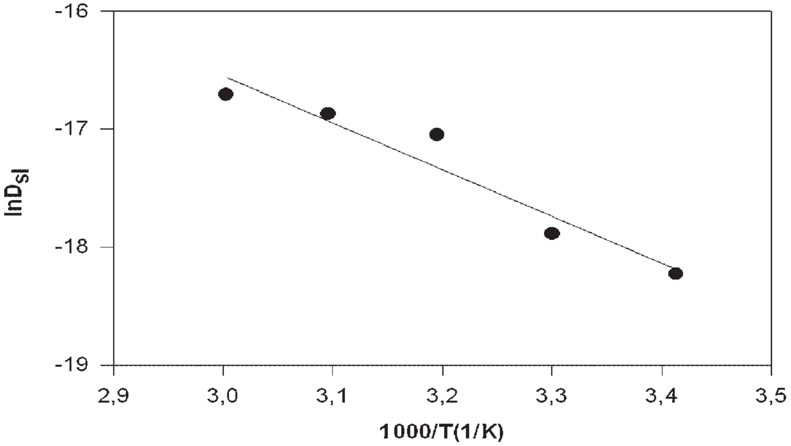

Figure 10.
Arrhenius treatment of desorption coefficients which produced ΔE_{sl} activation energy.

behavior of PAAm gel may be explained with its low T_g values. Two different values of activation energies may indicate two different regimes of swelling process. At low temperature region swelling needs much lower energy than at high temperature region, as expected.

Arrhenius treatment of the sorption coefficients produced two different sorption activation energies as shown in (Figure 9 a and b) from where ΔE_s and ΔE_l values were obtained and found to be 30, 9 kJmol^{-1} and 40, 6 kJmol^{-1} respectively.

Here one may suggest that P$_y$ sorption into PAAm gel is a two stage mechanism. At short times, sorption is slow and needs less energy; however at longer times sorption speeds up with higher energy need. In both cases sorption activation energies are much higher than swelling activation energies indicating that these two processes have different origins.

Arrhenius treatment of the desorption data in (Table 3) is presented in (Figure 10) from where corresponding activation energy; ΔE_{sl} is produced and found to be 34.8 kJmol^{-1}. Here it is seen that desorption and sorption activation energies are comparable in the given regions indicating that both processes need almost same energies to be performed.

Conclusion

The produced results have shown that the steady state fluorescence method can be used for real time monitoring of the swelling, sorption and desorption processes. In this powerful method in situ fluorescence experiments are easy to performed and inexpensive for providing us with the important dynamic parameters such as swelling, sorption and desorption coefficients and activation energies.

[1] M. Weiss, T. Van Vliet, A. Silberberg, *J. Polym. Sci. Polym. Phys. Ed.* **1979**, *17*, 2229.
[2] T. P. Hsu, D. S. Ma, C. Cohen, *Polymer* **1983**, *24*, 1273.
[3] T. Tanaka, S. T. Sun, Y. Hirokawa, S. Katayama, J. Kucera, Y. Hirose, T. Amiya, *Nature* **1987**, *325*, 796.
[4] T. Tanaka, *Phys. Rev. Lett.* **1978**, *40*, 820.
[5] T. Tanaka, D. Filmore, *J. Chem. Phys.* **1979**, *20*, 1214.
[6] J. Bastide, R. Duoplessix, C. Picot, S. Candau, *Macromolecules* **1984**, *17*, 83.
[7] M. Ilavsky, *Macromolecules* **1982**, *15*, 782.
[8] Y. Li, T. Tanaka, *J. Chem. Phys.* **1990**, *92*(2), 1365.
[9] M. Zrinyi, J. Rosta, F. Horkay, *Macromolecules* **1993**, *26*, 3097.
[10] S. Candau, J. Bastide, M. Delsanti, *Adv. Polym. Sci.* **1982**, *7*, 44.
[11] E. Geissler, A. M. Hecht, *Macromolecules* **1980**, *13*, 1276.
[12] M. Zrinyi, F. Horkay, *J. Polym. Sci. Polym. Ed.* **1982**, *20*, 815.

[13] A. K. Bajpai, M. Rajpoot, *J. App. Poly. Sci.* **2001**, *81*, 1238.

[14] M. Panayiotou, R. Freitag, *Polymer* **2005**, *46*, 615.

[15] M. P. Mullarney, T. A. P. Seery, R. A. Weiss, *Polymer* **2006**, *47*, 3845.

[16] Y. Liu, W. Liu, W. Chen, L. Sun, G. Zhang, *Polymer* *48*, 2665.

[17] S. Kara, Ö. Pekcan, *Polymer* **2000**, *41*, 3093.

[18] Ö. Pekcan, S. Kara, *Polym. Plast. Technol. Eng.* **2002**, *41*, 573.

[19] Ö. Pekcan, S. Kara, *Polymer* **2000**, *41*, 8735.

[20] S. Kara, O. Okay, Ö. Pekcan, *J. App. Polym. Sci.* **2002**, *86*, 3589.

[21] Ö. Pekcan, S. Kara, *Phase Transitions* **2003**, *76*, 601.

[22] M. Erdoğan, Ö. Pekcan, *Polymer* **2001**, *42*, 4973.

[23] Ö. Pekcan, Y. Yılmaz, O. Okay, *J. App. Poly. Sci.* **1996**, *61*, 2279.

[24] Ö. Pekcan, M. Erdogan, *European Polymer Journal* **2002**, *38*, 1105.

[25] G. A. Evingür, K. Karslı, Ö. Pekcan, *Int. J. Pharm.* **2006**, *326*(1–2), 7.

[26] J. Crank, "*The Mathematics of Diffusion*", Clarendon Press, Oxford **1970**.

[27] J. Crank, G. S. Park, "*Diffusion in Polymer*", Acad. Press, London **1968**.