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In situ steady state fluorescence (SSF) technique to study drying of PAAm hydrogels made of various cross-linker contents

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ABSTRACT

Drying experiments of polyacrylamide (PAAm) gels were performed using steady-state fluorescence (SSF) spectrometer. Pyranine (P) was introduced as a fluorescence probe and intensity of P from various cross-linker content gel samples was monitored. It was observed that the intensity of P increased during the in situ drying processes. Gravimetrical and volumetric experiments were also performed. An empirical model was derived and introduced to determine the desorption coefficient, D of water molecules from the drying PAAm gels. It is observed that D increased as the cross-linker content was increased.

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1. Introduction

Hydrogels may be conveniently described as hydrophilic polymers that are swollen by water, but do not dissolve in water. They are three-dimensional cross-linked polymeric structures that are able to swell in the aqueous environment. Cross-linked polymers capable of imbibing large volumes of water have found widespread applications in bioengineering, biomedicine, and food industry and water purification and separation process. Because of characteristic properties such as swelling ability in water, hydrophilicity, biocompatibility, and lack of toxicity, hydrogels have been utilized in a wide range of biological, medical, pharmaceutical, environmental applications [1–4].

The understanding of the phenomena occurring in the drying of these hydrogels is necessary for the designing of the entire process. Drying of hygroscopic solids is generally known to be a complex process because of simultaneous heat and mass transfer and variable physical properties of the materials [5]. Special polymers and hydrogels are highly hygroscopic and the shrinking and/or drying of these materials encompass many fields of technology. The quantity of bound water associated with the polymer varies as per the internal structure of the macromolecule. Monomer and cross-linking agent proportions are responsible for both the porous structure and the pore size of the gel. An acrylamide-derived hydrogel is a cross-linked network of polymer whose molecular weight is fairly high; it can absorb solvent (water), but is itself insoluble. During the water migration in the drying process, shrinkage corresponds simply to the compacting of solid mass. A diffusive drying model for the drying of highly shrinking materials like polyacrylamide (PAAm) gel and cellulosic paste have been reported [6]. Recently approximate models have been used by Coumans [7] to predict the drying kinetics for slab geometry.

Fluorescence methods, such as steady state spectroscopy, fluorescence anisotropy and transient fluorescence (TRF) measurements, have been shown to be quite effective in the investigation of the microscopic environment around a chromophore. The first fluorescence study on polymer gels was carried out by Horie et al. [8] to investigate the hydrophobicity and dynamic characteristics of cross-linked polystyrene with a dansyl probe. The photon transmission technique was used to study the drying of PAAm gels with various Bis contents [9]. Steady state and TRF techniques were applied to study the drying process of selected silane gels in oxygen free atmosphere. A kinetic model of drying was suggested and drying rate constants were determined [10]. The fast transient fluorescence (FTRF) technique was used in our laboratory to study gel swelling [11,12] and drying [13] processes. Recently we reported a study of drying mechanism of PAAm hydrogels by using the steady-state fluorescence (SSF) technique [14]. By combining the Stern–Volmer equation with an empirical drying equation the desorption coefficients, D, were determined for drying hydrogel at various temperatures. Gravimetrical technique was also introduced for measuring D values. The energies, ΔE,

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Table 1
Experimentally measured parameters of PAAm hydrogels for various Bis content during drying process

Bis[M]	$a_i \times 10^{-2}$ (m)	$a_f \times 10^{-2}$ (m)	$r_i \times 10^{-2}$ (m)	$r_f \times 10^{-2}$ (m)	$D_l \times 10^{-8}$ ($m^2\ s^{-1}$)	$D_w \times 10^{-8}$ ($m^2\ s^{-1}$)	$D_v \times 10^{-8}$ ($m^2\ s^{-1}$)
0.013	0.27	0.19	0.42	0.27	170	0.12	0.11
0.019	0.27	0.18	0.43	0.28	180	0.12	0.26
0.026	0.25	0.18	0.42	0.28	188	0.13	0.28
0.032	0.27	0.17	0.42	0.27	192	0.20	0.30

a_i: the initial disc thickness; a_f: the disc thickness in the final infinite equilibrium; r_i: the initial radius of the disc; r_f: radius of the disc in the final infinite equilibrium; D_l: fluorescence desorption coefficient; D_w: gravimetric desorption coefficient; D_v: volumetric desorption coefficient.

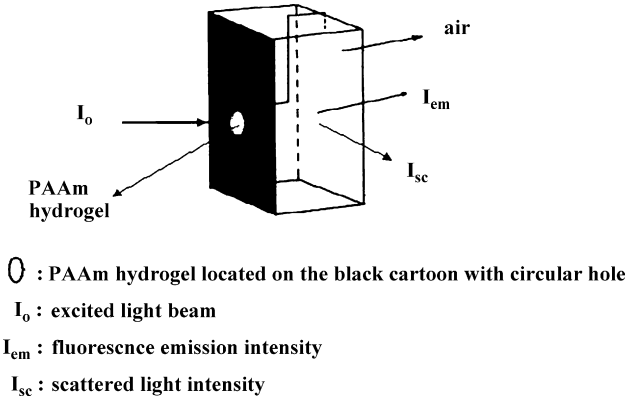

Fig. 1. The position of PAAm hydrogel in the fluorescence cell during drying in air. I_0 is excitation, I_{em} is emission and I_{sc} is scattered light intensities at 340 and 427 nm, respectively.

were measured for the drying processes and found to be 91.08 and 36.82 kJ mol^{-1} by fluorescence and gravimetrical methods, respectively.

In this work, we studied drying process of PAAm hydrogels prepared at various cross-linker contents by using the in situ steady-state fluorescence technique. Pyranine (P) was used as a fluorescence probe to monitor hydrogel drying. It was observed that the fluorescence intensity of pyranine increased as drying time was increased during the drying process. By combining the Stern–Volmer equation with the moving boundary model desorption coefficients, D were determined for drying hydrogels prepared at various cross-linker contents. Here our goal was to understand the structural effect on drying of PAAm hydrogel. Drying of various gels from loose structure (low cross-linker content) to dense structure (high cross-linker content) were studied at a given single temperature. Volumetric measurements were also introduced to see any difference from the gravimetrical observations. We expect from the findings of these observations that the fluorescence technique will be able to measure the behavior of the microstructure of the hydrogel during drying. Since pyranine molecules bounded to the polymer chains can monitor the drying process at a molecular level then one may expect that the segmental motion of the gel network can be studied by using fluorescence technique. On the other hand it is expected that the volumetric and gravimetric measurements may provide us with the information of the macroscopic and/or bulk behavior of the PAAm hydrogel.

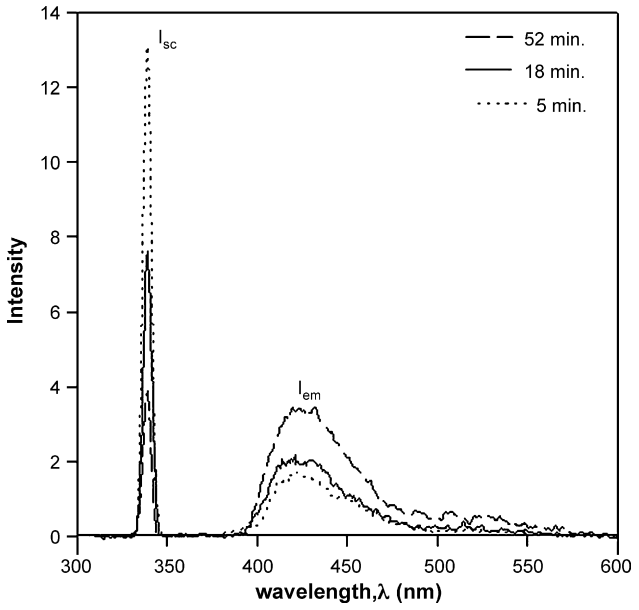

Fig. 2. Emission spectra of pyranine from the hydrogel prepared with 0.013 M Bis content during the drying process. Each curve indicates the drying times in different minutes.

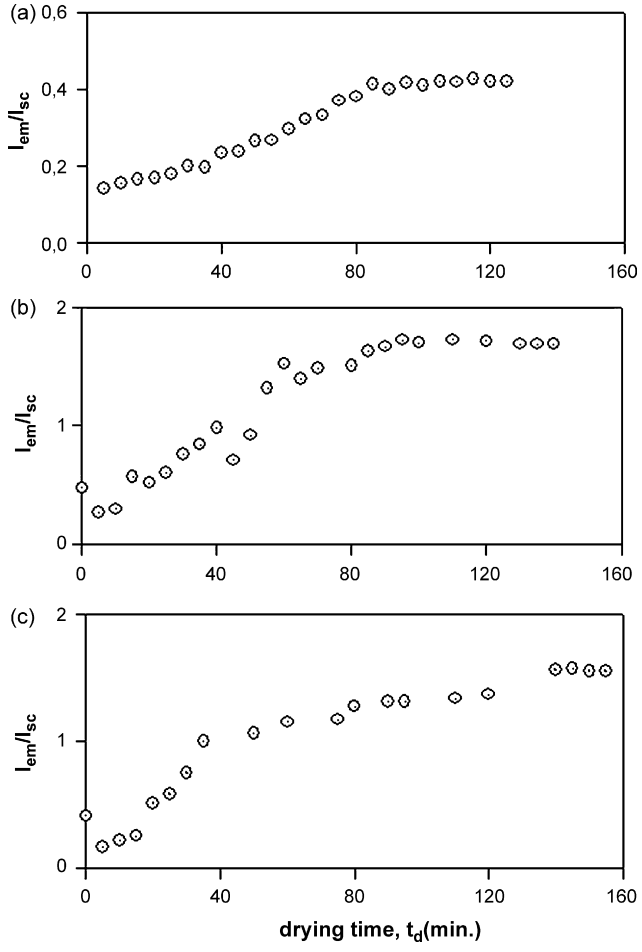

Fig. 3. Corrected fluorescence intensities of pyranine, I ($=I_{em}/I_{sc}$) vs. drying time, t_d during the drying process for (a) 0.013 M, (b) 0.026 M and (c) 0.032 M Bis content samples.

2. Experimental

2.1. Materials

Hydrogels were prepared by using 2 M AAm (Merck) and various Bis (Merck) by dissolving in 25 ml of water in which 10 μl 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 [15]. The drying experiments of disc shape PAAm hydrogels prepared with various cross-linker contents were performed in air. Details of the samples are listed in Table 1 (a_i, a_f, r_i, and r_f are the thicknesses and radii of disc shape gels before and after drying, respectively).

2.2. Fluorescence measurements

The fluorescence intensity measurements were carried out using a Model LS-50 spectrometer of PerkinElmer, equipped with a temperature controller. All measurements were made at the 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 drying time. Disc-shaped gel samples were placed on the wall of 1 × 1 quartz cell for the drying experiments. The position of the gel and the incident light beam for the fluorescence measurements are shown in Fig. 1 during drying of the hydrogel in air where I_0 and I_{sc} are the excitation and scattered light intensities, respectively. Here one side of the quartz cell is covered by black cartoon with a circular hole to collimate the light beam in order to minimize the effect related to the changes in the volume of the gel.

3. Results and discussion

Fig. 2 shows the emission spectra of pyranine in PAAm hydrogel during the drying process in air. It can be seen that as the water release is increased, fluorescence intensity, I_{em} increases and the scattered light intensity, I_{sc} decreases. Since the decrease in I_{sc} corresponds to the decrease in turbidity of the drying hydrogel, the corrected fluorescence intensity, I was defined as I_{em}/I_{sc}. The variations of I versus drying time, t_d during hydrogel drying for 0.013, 0.026 and 0.032 M Bis content samples are presented in Fig. 3(a–c). As the drying time, t_d, is increased, quenching of excited pyranines decrease due to increasing of water release from the drying hydrogel. It has also to be noted that quenching becomes less efficient at higher Bis contents. In order to quantify these results the collisional type of quenching mechanism may be proposed for the fluorescence intensity, I from the hydrogel sample during the drying process, where the following relation can be used [16]:

$$I^{-1} = I_0^{-1} + k_q \tau_0 [Q] \quad (1)$$

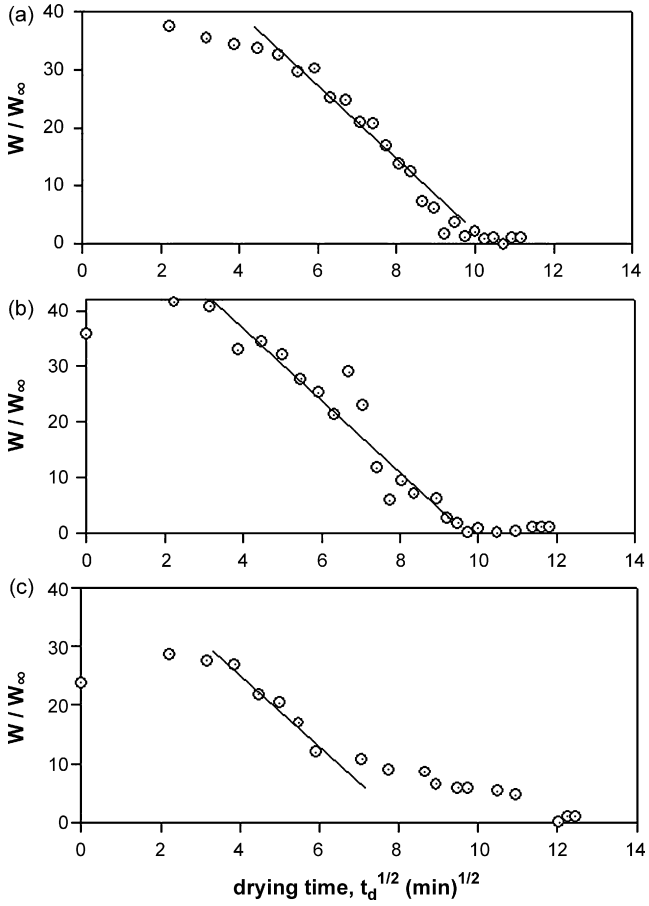

Fig. 4. Fit of the data by using Eq. (5) for PAAm hydrogels dried in air for (a) 0.013 M, (b) 0.026 M and (c) 0.032 M Bis content samples.

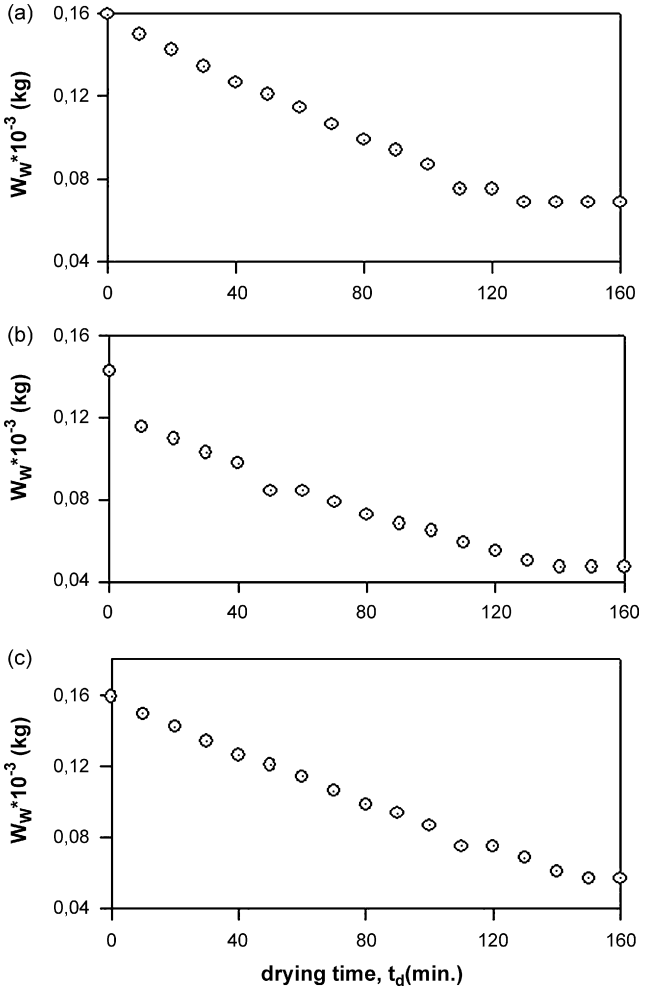

Fig. 5. The plots of the water release, W_w measured by gravimetrically, vs. drying time, t_d, for PAAm hydrogels dried in air for (a) 0.013 M, (b) 0.026 M and (c) 0.032 M Bis content samples.

here k_q is quenching rate constant, τ_0 is the lifetime of the fluorescence probe and Q is the quencher concentration and I_0 is the fluorescence intensity for zero quencher content. This relation is called Stern–Volmer equation.

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

$$I \approx I_0(1 - \tau_0 k_q[Q]) \tag{2}$$

if one integrates Eq. (2) over the differential volume (dv) of the hydrogel from the initial, a_0 to final a_∞ thickness, then reorganization of the relation produces the following useful equation:

$$W = \left(1 - \frac{I}{I_0}\right) \frac{\upsilon}{k_q \tau_0} \tag{3}$$

here the amount of water release, W is calculated over differential volume by replacing Q with W as

$$W = \int_{a_0}^{a_\infty} [W]\, \mathrm{d}\upsilon \tag{4}$$

here it is assumed that water molecules are the only quencher for the excited pyranine molecules. Where υ is the volume of the hydrogel at the equilibrium drying state, which can be measured experimentally. k_q was obtained from separate measurements by using Eq. (3) where the infinity equilibrium value of water release, W was used for each Bis content sample. Since τ_0 (=5 ns) is already known from the dry hydrogel, then W can be calculated from the measured I values at each drying step.

On the other hand, it has to be noted that drying phenomena in gels has not yet been completely modeled, because the drying process is not as simple as swelling, at least in water. In this work we have tried to simplify the drying process, but still the elastic forces of the gel are not considered. During drying, it is assumed that two regions exist in the gel, i.e. less concentrated region near the surface separates itself from the high concentrated region by a boundary which moves during drying towards the center of the gel. As the boundary moves, water molecules evaporate from the surface of the gel into air. Then, the behavior of W against t_d can be explained by considering a model in which diffusion occurs in two regions separated by a moving interface [17]. The moving interface can be marked by a discontinuous change in concentration as in the absorption by a liquid of a single component from a mixture of gases or by a discontinuity in the gradient of concentration as in the progressive freezing of a liquid. When the diffusion coefficient is discontinuous at a concentration c, i.e. the diffusion coefficient is zero below c and constant and finite above c; then the total amount, M_t of diffusing substance desorbed from unit area of a plane sheet of thickness a at time t, is given by the following relation [18]:

$$\frac{M_t}{M_\infty} = 2\left[\frac{D}{\pi a^2}\right]^{1/2} t^{1/2} \tag{5}$$

where D is a diffusion coefficient at concentration c_1. Here $M_\infty = ac_1$ is the equilibrium value of M_t. If one assumes that the diffusion

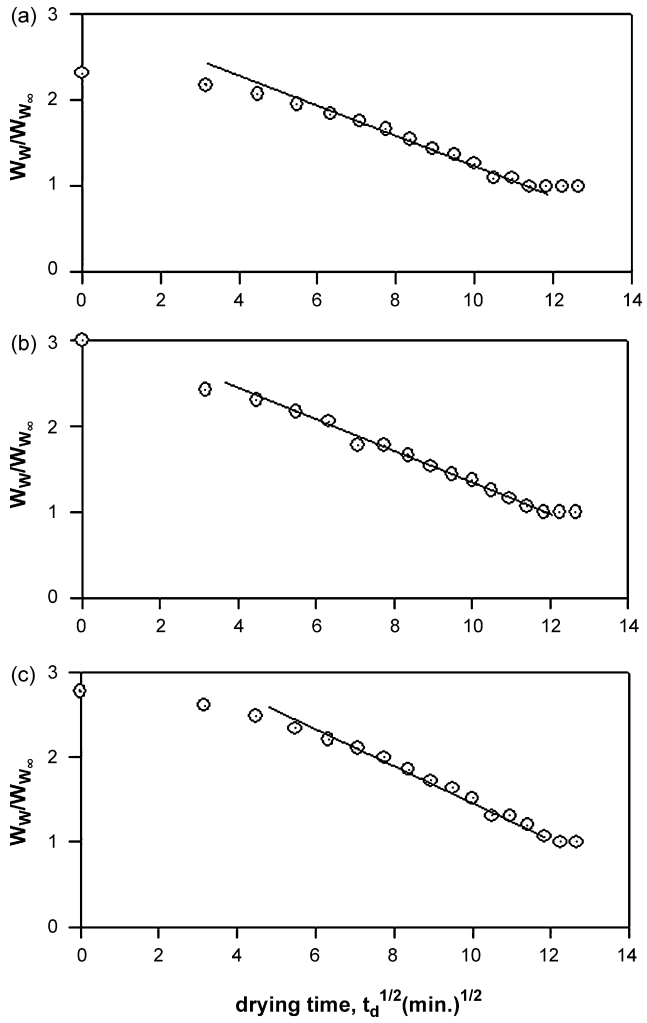

Fig. 6. Linear regressions of the data in Fig. 5 according to Eq. (6) for PAAm hydrogels dried in air for (a) 0.013 M, (b) 0.026 M and (c) 0.032 M Bis content samples.

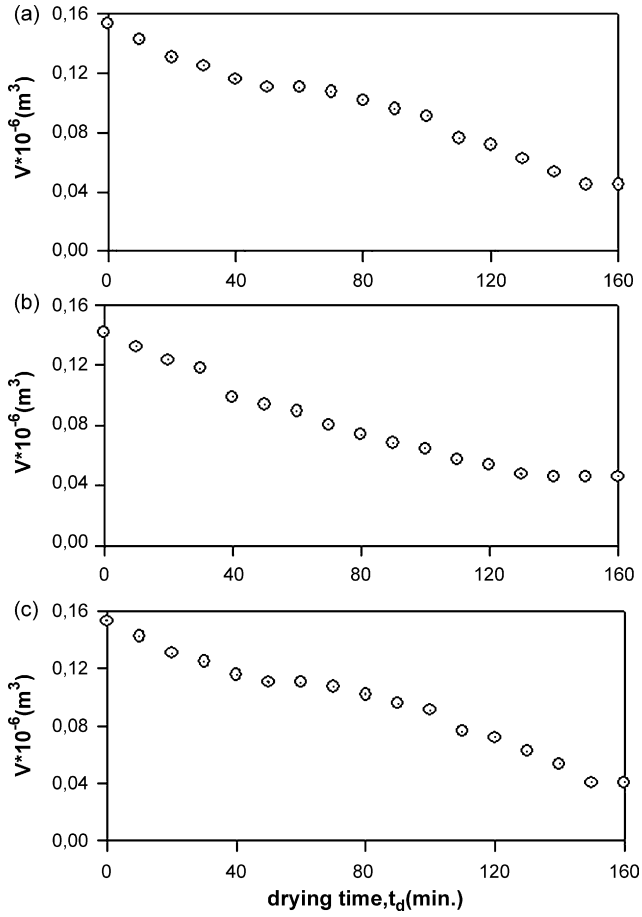

Fig. 7. The plots of the volume, v, variation vs. drying time, t_d, for PAAm hydrogels dried in air for (a) 0.013 M, (b) 0.026 M and (c) 0.032 M Bis content samples.

coefficient of polymer segments in the gel is negligible compared to the desorption coefficient, D of water vapor into air, then Eq. (5) can be written as follows:

$$\frac{W}{W_\infty} = 2\left[\frac{D}{\pi a^2}\right]^{1/2} t_d^{1/2} \quad (6)$$

here it is assumed that M_t is proportional to the amount of water molecules released, W at time, t_d. The plots of W versus $t_d^{1/2}$ at various Bis content samples are presented in Fig. 4 where the fit of the data produced the desorption coefficient, D_I which are listed in Table 1. It is seen that D_I values increased as the Bis content is increased as expected.

On the other hand, by using the gravimetrical methods water desorption was also measured from the drying PAAm hydrogel prepared at various Bis content. The plots of the data are presented in Fig. 5 for various Bis contents. The fits of water release, W_w versus $t_d^{1/2}$ are given in Fig. 6 for the hydrogel dried at 0.013, 0.026 and 0.032 M and the desorption coefficients, D_w were obtained from the slope of linear relation using Eq. (6). Measured D_w values are listed in Table 1, where it is observed that the desorption coefficient increases as the Bis content is increased.

The variations in volume, V of PAAm hydrogels during the drying process are also monitored. The plots of the volume V, versus drying time for PAAm hydrogels, dried into air are presented in Fig. 7.

The data in Fig. 7 are fitted to the following relation produced from Eq. (6):

$$\frac{V}{V_\infty} = 2\left(\frac{D}{\pi a^2}\right)^{1/2} t_d^{1/2} \quad (7)$$

here it is assumed, that the relation between W and V are linear. The fits are presented in Fig. 8, D_v volumetric desorption coefficient, are produced. Then, using Eq. (7) volumetric desorption coefficients D_v, were determined and listed in Table 1. Again, it is seen that D_v values increased as the Bis content is increased, similar to D_w behavior.

Here it is seen in Table 1 that, D_I values measured by using fluorescence technique are at least two orders of magnitude much larger than the values measured by volumetric and gravimetric techniques, which may predict the different physical behaviors of the hydrogel during drying. It is obvious that the fluorescence technique measure the behavior of the microstructure of the gel. In other words the segmental motion of the gel network is monitored by using fluorescence probe, because pyranine molecules are bounded to the polymer chains and monitors the drying process at a molecular level. However, volumetric and gravimetric measurements may provide us with the information of the macroscopic and/or bulk behavior of the gel. Here, it is understood that segmental organization in hydro gels are much faster than the bulk behavior during drying process.

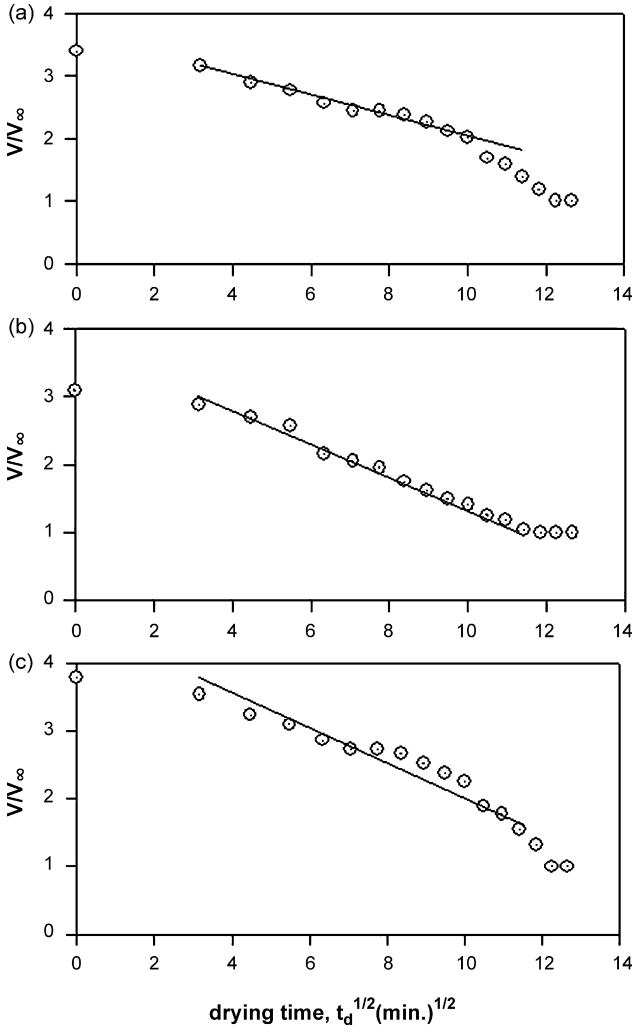

Fig. 8. Linear regressions of the data in Fig. 7 according to Eq. (7) for PAAm hydrogels dried in air for (a) 0.013 M, (b) 0.026 M and (c) 0.032 M Bis content samples.

4. Conclusion

These results have shown that the steady-state fluorescence technique, which is quite powerful and inexpensive, can be used for real-time monitoring of hydrogel drying processes. The empirical model was derived and used to determine the desorption coefficients (D_I, D_w, D_v) for the drying processes. Higher D_I values at high Bis content predicts that gel segments move much faster in densely formed gels than they do in loosely formed gels. It is also observed that D_w and D_v coefficients are found to be much larger at high Bis content gels. From this one can conclude that densely formed gels dry much faster than loosely formed gels.

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