# Swelling Kinetics and Diffusion Coefficients of Polyacrylamide Hydrogels *Via* Different Drying Methods

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**Abstract:** In the present study, polyacrylamide (PAAm) hydrogels were formed by copolymerization of acrylamide (AAm) and N,N' methylenebisacrylamide. The reaction is a vinyl addition polymerization initiated by a free radical generating system. N,N' methylenebisacrylamide, N,N,N',N'-tetramethylethylenediamine (TEMED) and ammonium persulfate (APS) were used as the cross linking agent, catalyzer and initiator, respectively. Hydrogels were dried with two drying methods: the former is the poor solvent method, the latter is the freze dryer method. The effects of the drying methods on swelling behavior were investigated as a function of time. A variety of hydrogel swelling kinetic modelling techniques were applied on the dynamic swelling rates of PAAm hydrogels. For all the hydrogels, the diffusion coefficient of kinetic parameters such as the diffusion mechanism (Fickian or non-Fickian mechanism), initial and equilibrium swelling ratios, the penetration rate of the solvent and diffusion coefficient were determined.

**Keywords:** Kinetic, diffusion coefficient, hydrogel, polyacrylamide.

## 1. INTRODUCTION

Hydrogels are three-dimensional hydrophilic polymers that absorb large amounts of water, swelling to form a solid gel while maintaining their physical structure without dissolving [1]. They have attracted considerable attention for their potential applications in medicine, pharmacy [2, 3], biotechnology [4], absorbent sanitary goods [5], agriculture [6] and water treatment [2]. There are several well-known methods to prepare porous hydrogels, including phase separation, foaming technique, emulsion-template synthesis, particulate leaching and freeze-drying [7, 8].

High swelling rate is an important property of hydrogels. They mainly need several hours to reach maximum absorption capacity. The slow swelling of dried hydrogels is due to the slow diffusion of water into the glassy matrix of the dried hydrogels [9].

Swelling is a continuous process of transition from a very fast swelling region to an equilibrium swelling region. It is well known that sorption processes for hydrogel-solvent systems frequently do not conform to the behavior expected from the classical theory of diffusion [10]. Although penetrant sorption by hydrogels may be described by Fickian transport with a concentration-dependent diffusion coefficient, this description is usually not successful with increasing time. Based on the Bajpai classification, two basic categories may arise [11]: the first is Fickian transport, which appears below the equilibrium swelling time. In this case, the polymer chains have high mobility and water penetrates easily in the polymer network. The second is non-Fickian diffusion, which appears above the equilibrium swelling time. In this situation, the polymer chains are not adequately mobile to permit urgent penetration of water into the polymer core [12]. Non-Fickian diffusion processes have been studied by many groups [10,13].

Poly(acrylamide) (PAAm) is an important and hydrophilic polymer for preparation of hydrogels. The common method to synthesise the PAAm hydrogels is the free radical crosslinking copolymerization of AAm monomer with multifunctional vinyl monomers [14]. PAAm hydrogels and their derivatives are the subject of many studies [15, 16]. PAAm hydrogels have proven capability of water absorption and biocompatibility with physiologic body fluids. The application of PAAm hydrogels in controlled release of agrochemicals and bioactive have been investigated [17, 18]. Researchers have reported on porous PAAm hydrogels [19, 20].

In this study, PAAm hydrogels were synthesized *via* free radical polymerization. The effects of the drying methods on swelling behavior were investigated as a function of time. Then network parameters such as the kinetic coefficient, solution diffusivity coefficient inside the network and diffusion mechanism were determined by using common kinetic models.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Acrylamide (AAm), the initiator, ammonium persulfate (APS), and the activator, N,N,N',N'-

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tetramethylethylenediamine (TEMED) were purchased from Merck (Darmstad, Germany) and used without further purification. The crosslinker, N,N'-methylenebisacrylamide (MBAAm) was supplied by Aldrich Chemicals (Milwaukee, US).

## 2.2. Methods

### *2.2.1. Synthesis of Polyacrylamide Hydrogels*

For a typical PAAm hydrogel synthesis, AAm (0.4868g) and MBAAm (13.2mg) were mixed in a dry 10mL filter flask to which 9mL deionized (DI) water was added. The monomer solution was gently swirled with a magnetic bar on a stirring plate until all reactants were completely dissolved. Following this, 0.5mL of APS solution (1.6% (w/v)) and 0.5mL of TEMED (5% (v/v)) were added to initiate polymerization, and the solution was swirled gently five or six times by hand to mix all reactants. The hydrogels were synthesized in airtight glass tubes. Polymerization was conducted in a water bath at 25°C for 24 h. Then, the synthesized hydrogels were removed from the tubes by breaking the glass tubes. The synthesized gels were immersed in deionized (DI) water for a week, with water changed two times a day to remove any unreacted monomers.

### *2.2.2. Drying of Polyacrylamide Hydrogel*

#### 2.2.2.1. Poor Solvent Method

Acetone solutions (20, 40, 60, 80, 100% (v/v)), 100ml were prepared in 250ml beakers. At first, the hydrogel was immersed in the 20% acetone solution. The weight of the sample was measured at least twice a day until it attained a constant value. The sample that attained constant value was immersed in the 40, 60, 80, 100% acetone solutions, respectively.

#### 2.2.2.2. Freeze Dryer Method

The hydrogel was frozen in the freezer for 24 hours at -18°C. Then, the sample was dried for 24 hours in the freeze dryer.

#### 2.2.2.3. Swelling Measurements of Polyacrylamide Hydrogels

Swelling behavior of the hydrogels was followed by gravimetric measurements. Each dry hydrogel was immersed into adequate deionized water (200ml) at room temperature, and was weighed until reaching the swelling equilibrium. Degree of swelling (*S*) was calculated with the following equation:

$$S = \frac{m_t - m_0}{m_0}$$

Where $m_t$ is the mass of the swollen gel at time t and $m_0$ is the mass of the dry gel.

The equilibrium degree of swelling $S_{eq}$, after the hydrogels had swollen to a maximum in the swelling media was calculated with the following equation:

$$S_{eq} = \frac{m_{max} - m_0}{m_0}$$

Here, $m_t$ is the mass of the swollen hydrogel sample at time t, $m_0$ is the initial dry mass of the hydrogel sample and $m_{max}$ is the mass of the swollen hydrogel sample at equilibrium.

For the swelling studies, an average value of four replicates was taken.

#### 2.2.2.4. SEM Analysis of Polyacrylamide Hydrogels

After being sputter-coated with gold, SEM micrographs were obtained. SEM analyses were carried out by using an ESEM-FEG/EDAX Philips XL-30.

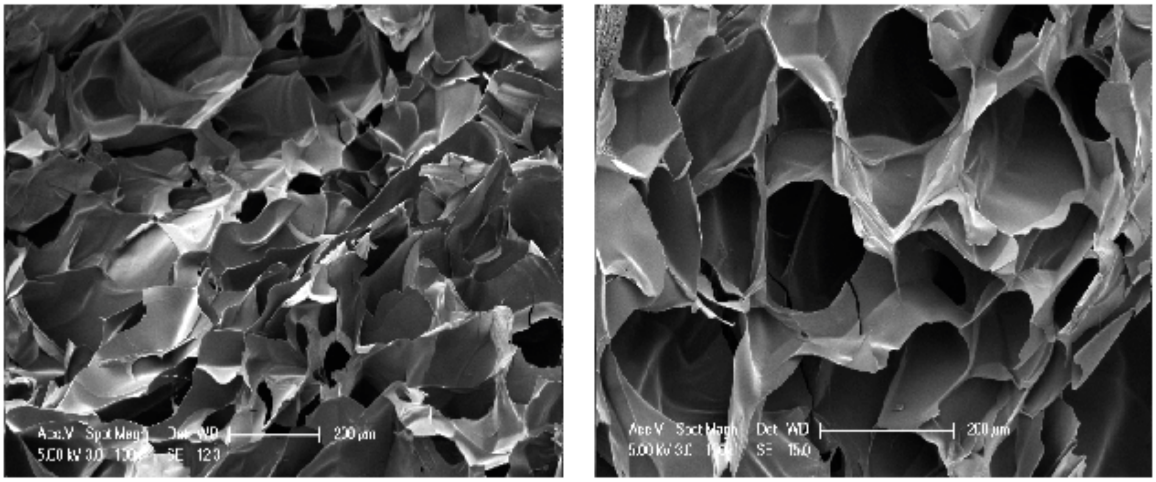
## 3. RESULTS AND DISCUSSION

## 3.1. SEM Analysis

PAAm hydrogels were prepared by polymerization of AAm/BAAm monomer solution in aqueous medium in the presence of APS and TEMED. The hydrogels were dried with two drying methods: the first is the poor solvent method, and the second is the freeze dryer method.

The surface morphology of the hydrogel was examined by SEM analysis. SEM images of PAAm hydrogels are shown in Figure **1**.

It is quite clear that the dried PAAm hydrogel with the poor solvent method (Figure **1a**) exhibited a somewhat porous structure but mostly had closed cells with few 0-50 micrometer-sized open cells. In contrast, it is observed that dried PAAm hydrogel with the freeze dryer method had a large number of open pores. Moreover, the porous structure consists of 150-200 micrometer-sized open cells. When analyzing the impact of drying methods on hydrogels, compared to dried PAAm hydrogels with the poor solvent method, it was found that the amount and size of the pores of



a)

b)

**Figure 1:** SEM images of, **a)** dried PAAm hydrogel with poor solvent method, **b)** dried PAAm hydrogel with the freeze dryer method.

dried PAAm hydrogels with the freeze dryer method are greater. Thus, it is identified that dried PAAm hydrogel with the freeze dryer method is superior to the other method with regard to surface properties.

### 3.2. Swelling Analysis

The swelling behavior of the PAAm hydrogels was investigated in deionized water at 25$^o$C. The effects of the drying methods on swelling behavior were investigated as a function of time.

Figure **2** illustrates the equilibrium of water content and dynamic swelling behavior of hydrogels as a function of the drying methods. As presented in this figure, all hydrogels reached equilibrium swelling at three days. The water absorbency of the hydrogel which was dried with the freeze dryer method, is more than for the other hydrogel. While the equilibrium swelling of drying hydrogel with the freeze dryer method is 25.8, the equilibrium swelling of drying hydrogel with the poor solvent method is 6.8.

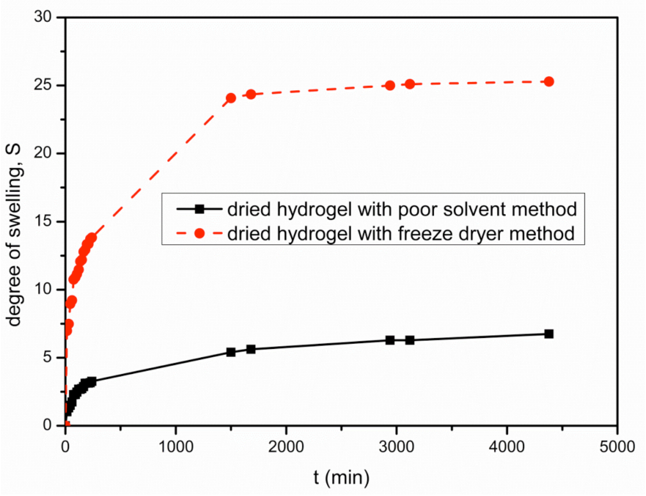


**Figure 2:** Swelling behavior of PAAm hydrogels in deionized water (0-4320 minutes; 25$^o$C).

This may be attributed to the fact that the dried hydrogel with the freeze dryer method makes the hydrogel structure highly porous (Figure **1b**) and results in a high water uptake. Also, the hydrogel absorbing a higher amount of water may be due to increased pore size. The rate of water uptake in porous hydrogels is higher than that of non-porous hydrogels. An increase in the rate of absorption would be expected from the increase in surface area with increasing porosity of the hydrogels.

In order to study the effect of the drying methods on the kinetics of the water uptake of PAAm hydrogels, water uptake data was fitted using the following models.

#### *3.2.1. Model I*

$$S / S_{eq} = kt^n$$

In Model I, *S* is the degree of swelling (or mass of solvent imbibed) at any time *t*, *Seq* is the degree of swelling when equilibrium is reached (or amount of solvent imbibed at equilibrium), *k* is the swelling constant characteristic of polymer network and *n* is the diffusional exponent characterizing the mechanism of diffusion of solvent into the network. For cylindrical geometry, the value of diffusional exponent *n* as 0.45

signifies a Fickian diffusion mechanism, while $n \geq 0.89$ indicates a Case II diffusion mechanism and the value of $n$ in the range $0.45 < n < 0.89$, indicates that the diffusion mechanism is anomalous or non-Fickian, where both diffusion and polymer relaxation control the overall rate of water uptake [21].

The previously discussed power law equation, even though it effectively describes the major portion of the swelling behavior, fails to give a precise analysis above $S/Seq = 0.60$.

**Table 1: Effect of the Drying Methods on the Swelling Kinetic Parameters of PAAm Hydrogels**

| t (min) | $S/S_{eq}$ (Dried Hydrogel with Poor Solvent Method) | $S/S_{eq}$ (Dried Hydrogel with Freeze Dryer Method) |
|---|---|---|
| 0 | 0 | 0 |
| 60 | 0.2590 | 0.3640 |
| 120 | 0.3989 | 0.4532 |
| 180 | 0.4626 | 0.5112 |
| 240 | 0.4835 | 0.5464 |
| 1500 | 0.8009 | 0.9520 |
| 1680 | 0.8319 | 0.9623 |
| 2940 | 0.9317 | 0.9880 |
| 3120 | 0.9305 | 0.9925 |
| 4380 | 1 | 1 |

From Table **1**, the plots of log($S/Seq$) vs time log (t) for PAAm hydrogels were drawn and it is obvious that the diffusional exponent n value was obtained at $n < 0.5$ for all hydrogels (Figure **3** and Table **2**).

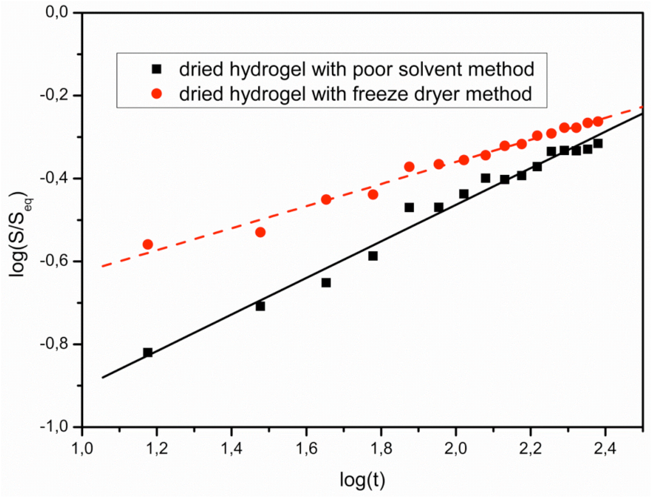


**Figure 3:** Plot of log ($S/S_{eq}$) *vs* log (t) for PAAm hydrogels in deionized water (0-270 minutes; 25°C).

The values of diffusional exponent $n$ and diffusion constant $k$ determined from the slope and intercept of the lines are reported in Table **2** for the swelling studies conducted.

**Table 2: n and k Values of PAAm Hydrogels for 0-240 Minutes**

| Sample | n | k | Model I Error |
|---|---|---|---|
| Dried hydrogel with poor solvent method | 0.4413 | 0.04508 | 0.04981 |
| Dried hydrogel with freeze dryer method | 0.2663 | 0.12806 | 0.02916 |

It can be seen from the tables that the value of n decreased with the increase in both pore size and number in the hydrogel structure. This indicates clearly that the solvent transport mechanism of all hydrogels becomes the Fickian diffusion mechanism. Fickian diffusion refers to a situation where the water penetration rate in the gels is less than the polymer chain relaxation rate. In this case, the polymer chains have high mobility and water penetrates easily in the polymer network. Moreover, little error in Model I shows that the model is effectively used.

### *3.2.2. Model II*

$$t/S = A + Bt$$

Model II represents second order kinetics which can be used to explain the extensive swelling of the hydrogels [22]. Here, $S$ is the degree of swelling at time t, $A = 1/(dS/dt)_0$, is the reciprocal of the initial swelling rate of the hydrogel and $B = 1/S_{max}$ is the inverse of the equilibrium swelling of the hydrogel [23].

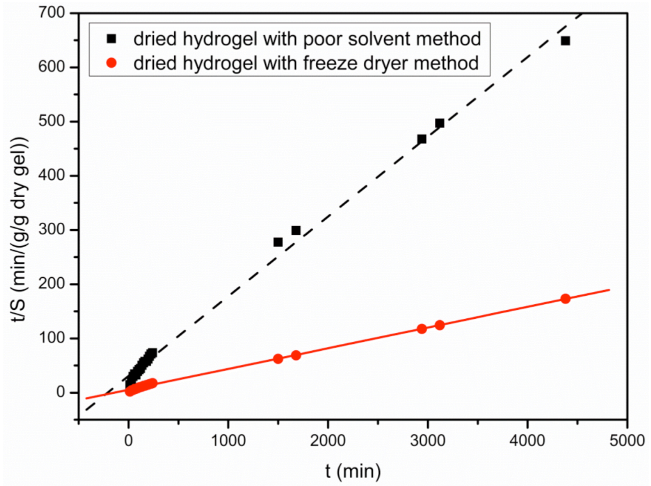


**Figure 4:** Plot of t/S *vs* t for PAAm hydrogels in deionized water (0-4320 minutes; 25°C).

Figure **4** shows the linear regression of representative regression swelling curves fitted to Model II for PAAm hydrogels for 4320 minutes. Similar swelling curves were obtained for hydrogels using different drying methods.

The initial swelling rate and the values of maximum swelling of the hydrogels were calculated from the intersection and slope of the lines and the values are presented in Table **3**.

**Table 3: Effect of drying methods on swelling kinetic parameters of PAAm hydrogels in Model II for 0-4320 minutes.**

| Sample | $S_{eq}$ | $S_{max}$ | Model II Error | $(dS/dt)_0$ |
|---|---|---|---|---|
| Dried hydrogel with poor solvent method | 6.7467 | 6.7935 | 0.17439 | 0.03275 |
| Dried hydrogel with freeze dryer method | 25.2981 | 26.7180 | 0.20821 | 0.18216 |

According to Table **3**, compared to dried PAAm hydrogels with the poor solvent method, it is found that the initial swelling rate of dried PAAm hydrogels with the freeze dryer method is greater. Thus, it is identified that dried PAAm hydrogel with the freeze dryer method is superior to the other method with regard to initial swelling rate. Moreover, from this table a reasonable agreement between the experimental values of maximum equilibrium swelling ratio *Seq* and the values predicted by Model II, within the accuracy of the experimental data, is observed.

In order to compare the relative performance of these models, the mean relative quadratic error was calculated for all three models listed in Tables **2-3**:

$$Model\ Error = \sqrt{\frac{\sum\left(\frac{S_{cai} - S_{\exp}}{S_{\exp}}\right)^2}{N-1}}$$

### 3.3. Diffusion Coefficient of Hydrogels

For hydrogel characterization, the short time approximation method was used for the calculation of diffusion coefficient D for PAAm hydrogels. The short time approximation method is valid for the first 60% of swelling of the crosslinked polymers in a chosen solvent. The following equation, applicable to a cylindrical shape, was used to calculate the diffusion coefficient *D*:

$$F = 4\left[\frac{Dt}{\pi L^2}\right]^{\frac{1}{2}} - \pi\left[\frac{Dt}{\pi L^2}\right] - \frac{\pi}{3}\left[\frac{Dt}{\pi L^2}\right]^{\frac{3}{2}} + \ldots$$

where *D* is the diffusion coefficient in cm$^2$ min$^{-1}$, *t* is the time in seconds**,** *L* is the radius of the cylindrical polymer sample in cm, and *F(S/S$_{eq}$)* denotes the fraction of solvent diffusing into the hydrogel at time *t*.

For all PAAm hydrogels, F vs t$^{1/2}$ plots were obtained and the coefficient of diffusion was estimated from the slope of the curves. Some representative plots are shown in Figure **5**.

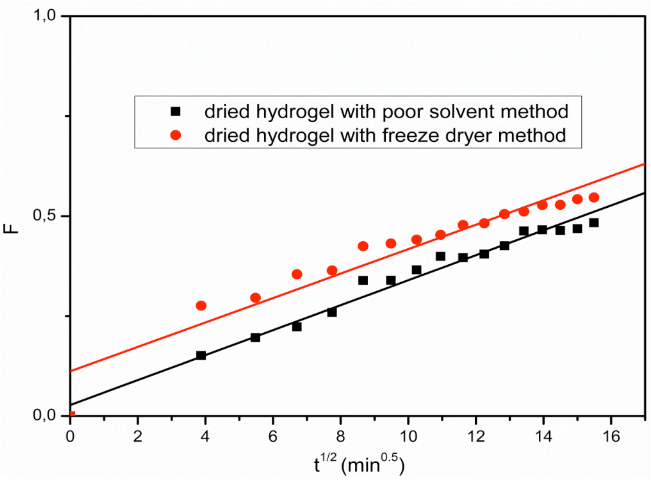


**Figure 5:** Plot of F *vs* t$^{1/2}$ for PAAm hydrogels in deionized water (0-240 minutes; 25°C).

The values of D obtained from $F = 4[(Dt)/(\pi L^2)]^{1/2}$ are listed in Table **4**.

**Table 4: Diffusion Coefficient of PAAm Hydrogels for 0-240 Minutes**

| Sample | D ($10^{-5}$ cm$^2$ /min) |
|---|---|
| Dried hydrogel with poor solvent method | 3.05815 |
| Dried hydrogel with freeze dryer method | 11.6899 |

According to Table **4**, it is found that the diffusion coefficient of dried PAAm hydrogels with the freeze dryer method is much higher than the diffusion coefficient of dried PAAm hydrogels with the poor solvent method. This result clearly shows that porous structure greatly influences the diffusion coefficient. It is found that increased porous structure increases the water absorbing capacity of hydrogels.

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