

An experimental study of the swelling behaviour of spherical hydrogel in water and the formulation of a theoretical model for its explanation

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Abstract:

The mechanism of variation of mass and volume, through the absorption of water, by the most commonly used and abundantly available spherical hydrogel beads of various colours has been studied. Immersing the beads in distilled water, both mass and volume were measured at regular intervals. By an analysis of mass-versus-time data, using standard theoretical methods, the mechanism of diffusion of water has been studied. Relaxation controlled transport was found to be the predominant process of diffusion of water into the materials under study. The diffusion coefficient has been determined for hydrogels of different colours. Various swelling related parameters such as equilibrium water content, equilibrium swelling ratio, characteristic time, initial rate of water absorption etc. were determined for these hydrogels. The maximum attainable mass and the maximum number water molecules that can be attached to active polymer sites in a single bead have been calculated. In this regard, the number of such active sites per unit volume and mass of dry hydrogel was determined. A theoretical model has been developed, based on the consideration of water absorption through the occupation of vacant polymer sites in a highly porous hydrogel. Considerations of cylindrical and spherical pores in this model predicted almost the same swelling behaviour. Expressions relating mass and volume with time have been formulated and they agreed well with experimental observations. The dependence of characteristic time (τ) upon structural parameters have been established. Values of swelling related parameters have been determined by a numerical fitting of theoretical model to experimental data. The agreement of experimental findings with theoretical predictions has been depicted graphically.

Keywords: *super-absorbent polymer, hydrogel swelling, diffusion, porous hydrogel, mass swelling ratio, volume swelling ratio, equilibrium water content, equilibrium swelling ratio*

Introduction:

Some superabsorbent polymer gels, also known as hydro gels or water crystals, have attracted enormous attention from a large community of researchers belonging to a wide variety of fields, due to their immense potential for application in a number of ways [1]. Hydrogels have plenty of applications in agriculture, drug delivery, micro-fluid systems, contact lenses, industrial wastewater treatments, wound management and tissue engineering [1,2,3]. Hydrogels may be used in sensing applications in which the swelling or de-swelling of the material is converted via a transducer into a measurable signal [4]. The sensitivity of hydrogels to a large number of chemical and physical factors like temperature, light,

electrical voltage, pH, ionic strength, biological, and chemical agents make them suitable for a broad range of applications [5]. Miniaturized hydrogel objects are strong candidates for sensors and actuators in micro-electro-mechanical systems (MEMS) technology [3]. Electro-responsive ionic polymer gels have been employed for designing dust wipers, miniature robotic arms etc [6]. Typically these hydrogels at equilibrium comprise 60–90 % fluid and only 10–30 % polymer [7, 8]. Due to characteristic properties such as expansion in water, high water content and elastic nature similar to natural tissues, biocompatibility and lack of toxicity, hydrogels are being utilized in a wide range of biological, medical, pharmaceutical and environmental applications [9-12].

Hydrogels are three-dimensional networks which are formed by copolymerization of monomers with cross linking agents [13]. These gels are able to absorb considerable amounts of water due to their hydrophilic characteristics [14, 15]. According to Pal et al, hydrogel can be defined as a cross linked polymeric network having the capacity to hold water within its porous structure [2]. The water holding capacity of the hydrogels arise mainly due to the presence of hydrophilic groups, viz. amino, carboxyl and hydroxyl groups, in the polymer chains. According to Hoffmann, the amount of water present in a hydrogel may vary from 10% to thousands of times of its weight in the dry state [16].

In the present article we have described a study of the swelling properties of hydrogel in aqueous medium with regard to both mass and volume. In this regard, a parameter called mass swelling ratio (*MSR*), denoted by $q(t)$ in this article, has been calculated [1]. This parameter is defined in the following way:

$$MSR = q(t) = \frac{M(t) - M_0}{M_0} \quad (1)$$

Here $q(t)$, $M(t)$ and M_0 are respectively the mass swelling ratio, the mass of hydrogel at any time t and the mass of hydrogel in its dry state.

When the mass no longer changes with time for a hydrogel in water, it is said to be in chemical equilibrium with the solution in which it is immersed. The parameters called equilibrium swelling ratio (*ESR*) and the equilibrium water content (*EWC*) are calculated using the following equations (2) and (3), respectively [1].

$$ESR = q_e = \frac{M_{\max} - M_0}{M_0} \quad (2)$$

$$EWC = \frac{M_{\max} - M_0}{M_{\max}} \quad (3)$$

In the above equations M_{\max} denotes the mass of the hydrogel when it is in perfect equilibrium with the solution in contact. It is the maximum attainable mass of a hydrogel bead. The highest value of $q(t)$ or *MSR* is q_e or *ESR*.

The swelling properties of hydrogels are often found to obey some mathematical relations given below [7].

$$\frac{q}{q_e} = kt^n \quad (4)$$

$$\frac{t}{q} = A + Bt \quad (5)$$

$$q = q_e (1 - e^{-t/\tau}) \quad (6)$$

Water molecules migrate into the polymer network by diffusion. In equation (4), the constant k is the swelling constant, characteristic of polymer network, and n is the diffusional exponent characterizing the mechanism of diffusion of the solvent into the network. Peppas et al. were the first to give an introduction to these equations [18]. For hydrogel, $n = 0.45$ indicates Fickian diffusion, $0.50 < n < 0.89$ indicates anomalous transport (non-Fickian) and $n \geq 0.89$ implies CASE II (relaxation-controlled) transport [7, 17]. This power law equation, fails to give a precise analysis above $q/q_e = 0.6$ [19]. To obtain a better model beyond 60%, Berens-Hopfenberg proposed a model represented by equation (6) [20]. This is a Voight-based equation where τ is smaller for higher rates of solvent penetration. Equation (5) represents a model based on second order kinetics that can be used to explain the swelling of hydrogels [7, 21, 22]. Here, $A = [1/(dq/dt)]$ at $t = 0$ and $B = 1/q_e$ where $q \rightarrow q_e$ at $t \rightarrow \infty$. Thus, the initial value of dq/dt is $1/A$.

For the case of anomalous transport, Peppas et al. developed the following model to describe the behaviour of dynamically swelling hydrogels [17, 23]:

$$\frac{q}{q_e} = k_1 t + k_2 t^{1/2} \quad (7)$$

This expression describes the swelling mechanism in terms of relaxation-controlled transport process $k_1 t$, and the diffusion-controlled process $k_2 t^{1/2}$.

Diffusion coefficient of water moving through hydrogels is given by [24, 25]:

$$D = \pi R_0^2 \left(\frac{k}{4} \right)^{1/n} \quad (8)$$

Here D is the diffusion coefficient of water ($cm^2 \text{ min}^{-1}$) and R_0 is the radius of the dry gel.

By fitting equation (6) numerically to the experimental data, one can determine the values of τ and q_e . For many cases it would be very difficult to determine q_e experimentally, because the experiment has to be continued for a very long time for that purpose.

Most of the studies discussed above were centered around the effect of temperature, pH, and concentration etc. of the solution on the nature of hydrogel swelling. In the present study, we have developed a theoretical formulation leading to the expression of equation (6) and thereby we have derived expression for q_e and τ , exploring their relation with certain physical parameters. Instead of using the standard theories of diffusion, we have described absorption of water in terms of the phenomenon of attachment of ionized water molecules to charged sites on the polymer chains and thereby causing a volume expansion of hydrogel.

Materials and Methods:

We procured spherical hydrogel beads of various colours, most abundantly available and most widely used in Calcutta, from a standard source. The main ingredient of these gels are poly-acrylate or poly-acrylamide. These non-toxic, biodegradable products are mostly used for home decoration, crafts, floral and candle arrangements and also as water retaining agents for plants used in horticulture. Commonly known as Magic Pearl Jelly or Crystal Soil,

these multicolored beads are a kind of Super Absorbent Polymer (SAP) which are also known as water gels, crystal pearls, water pearls, magic crystals, flora gels, decorative jelly. The swollen gels can be perfect substitutes for soil required for plants used for floral decoration. Apart from decorative function, they also reduce plant watering by up to 50% due to their ability of retaining water, which is almost 200 times their dry weight. Furthermore, it is able to repeatedly absorb and release water for many times. Superabsorbent polymers (SAP) are now commonly made from the polymerization of acrylic acid blended with sodium hydroxide in the presence of an initiator to form a poly-acrylic acid sodium salt (referred to as sodium polyacrylate). This polymer is the most common type of SAP made in the world today [26, 27].

In our experiment, these spherical beads of hydrogel were kept immersed in distilled water and the mass and volume of each bead were measured at intervals of fifteen minutes. Each time, after taking out from water, a bead is put in contact with blotting paper for removing water from its surface. The radius of a bead was measured by a screw gauge having an accuracy of 0.001 cm and the mass was measured by a digital weighing machine having an accuracy of 0.001gm. Stop watches, having an accuracy of one second, were used for time measurement. We studied the swelling behaviour of beads of white, yellow, orange, red, pink and green coloured hydrogels, having initial diameters of 4.80, 3.80, 2.80, 2.40, 2.38, and 2.40 mm respectively and with initial masses of 0.036, 0.022, 0.023, 0.010, 0.011 and 0.011 gm respectively. These are denoted by sample names A,B,C,D,E and F respectively in the present article.

Characterization by Analysis of Experimental Data:

Using the equations (1), (2) and (6), the *rate of change in swelling ratio* can be expressed as,

$$\frac{dq}{dt} = \frac{1}{M_0} \frac{dM(t)}{dt} = \frac{q_e}{\tau} e^{-t/\tau} \quad (9)$$

Thus, the value of dq/dt at $t = 0$ is can be written as,

$$\left[\frac{dq}{dt} \right]_{t=0} = \frac{1}{M_0} \left[\frac{dM}{dt} \right]_{t=0} = \frac{q_e}{\tau} \quad (10)$$

Following equation (4), we have plotted $\log(q/q_e)$ as a function of $\log(t)$ to determine the values of n and k from slope and intercept respectively. These plots, along with theoretical best fits, are shown in Figure2. The values of k and n are listed in TABLE 1. The values of n clearly indicate that relaxation-controlled diffusion process takes place for all our samples.

Sample	M_0 (gm)	M_{\max} (gm)	$q_e = \frac{M_{\max} - M_0}{M_0}$	τ (minutes)	$\left[\frac{dq}{dt} \right]_{t=0} = \frac{q_e}{\tau}$ (min ⁻¹)	k	n
A	0.036	5.578	153.953	242.891	0.634	0.0033	1.005
B	0.022	5.033	227.755	318.948	0.714	0.0019	1.008
C	0.023	5.708	247.160	276.532	0.894	0.0016	1.043
D	0.010	1.610	159.966	137.062	1.167	0.0068	0.939
E	0.011	1.707	154.226	132.694	1.162	0.0073	0.929
F	0.011	1.472	132.838	127.986	1.038	0.0070	0.943

Equations (4) and (6) have been found to have a much better agreement with experimental data, compared to the equation (5). Using equations (1), (2), (6) one can formulate the following expression of water intake $I(t)$.

$$I(t) = M(t) - M_0 = (M_{\max} - M_0)(1 - e^{-t/\tau}) \quad (11)$$

The curves in Figure 1 are the best fits of equation (11) to the experimental data regarding mass variation. The theoretical curves, based on equation (11), agree very well with experimental data for different samples of hydrogels.

By this numerical curve fitting we have determined the values of M_{\max} and τ and thereby calculated q_e , listed in TABLE 1. The initial rates of change of q are also shown in the same table.

The rate of water intake (RI), calculated from equation (11), is written as,

$$RI(t) = \frac{dI(t)}{dt} = \frac{dM(t)}{dt} = \frac{M_{\max} - M_0}{\tau} e^{-t/\tau} \quad (12)$$

Therefore, the initial rate (RI_0) is given by,

$$RI_0 = [RI]_{t=0} = \frac{M_{\max} - M_0}{\tau} \quad (13)$$

The values of diffusion coefficients (D), calculated on the basis of equation (8), are shown in TABLE 2. This table contains the values of EWC , ESR and RI_0 for different samples. Number of active sites (N) in a bead is also shown in the same table, taking the mass of a water molecule $m = 2.99146 \times 10^{-23}$ gm.

It is an important experimental observation that the values of EWC are very close to one another for different hydrogels. Using equation (3), EWC can be defined in the following way.

$$EWC = \frac{\text{mass of water content at equilibrium}}{\text{mass of dry hydrogel} + \text{mass of water content at equilibrium}} \quad (14)$$

Our data shows that its value is very close to 0.99.

Thus, one may infer that a principal governing factor of the swelling process drives it towards the maximization of EWC . According to equation (2), ESR can be defined in the following way.

$$ESR = \frac{\text{mass of water content at equilibrium}}{\text{mass of dry hydrogel}} \quad (15)$$

Combining the equations (14) and (15) we can write,

$$EWC = \frac{ESR}{1 + ESR} \quad (16)$$

TABLE 2					
Sample	D (cm^2/min)	EWC	ESR	RI_0	$N = \frac{M_{\max} - M_0}{m}$
A	7.360×10^{-5}	0.9935	153.953	0.0228	1.853×10^{23}
B	4.238×10^{-5}	0.9956	227.756	0.0157	1.675×10^{23}
C	2.438×10^{-5}	0.9959	247.160	0.0206	1.900×10^{23}
D	2.055×10^{-5}	0.9938	159.966	0.0117	5.347×10^{22}
E	2.052×10^{-5}	0.9936	154.226	0.0128	5.671×10^{22}
F	2.046×10^{-5}	0.9925	132.838	0.0114	4.885×10^{22}

Dividing equation (11) by M_{\max} we get,

$$\frac{M(t) - M_0}{M_{\max}} = \left(\frac{M_{\max} - M_0}{M_{\max}} \right) (1 - e^{-t/\tau}) = EWC (1 - e^{-t/\tau}) \quad (17)$$

The above equation shows that, as time goes on, the ratio $[M(t) - M_0] / M_{\max}$ approaches *EWC* asymptotically. The water molecules get attached to the hydrophilic sites of the polymer by hydrogen bonding and the number of such sites should be proportional to the dry mass of hydrogel. The maximum number of molecules that can be attached to the hydrogel is likely to be a function of its dry mass. Let M_w and M_0 denote the masses of equilibrium water content and dry gel respectively. Their relation can be expressed in the following form.

$$M_w = f(M_0) \quad (18)$$

Using equations (14) and (18) we can write,

$$EWC = \frac{M_w}{M_0 + M_w} = \frac{f(M_0)}{M_0 + f(M_0)} = \frac{f(M_0)/M_0}{1 + f(M_0)/M_0} \quad (19)$$

Comparing equation (19) with equation (16) we conclude that,

$$ESR = f(M_0) / M_0 \quad (20)$$

The function in equation (18) should be such that $f(M_0) = 0$ for $M_0 = 0$. The simplest functional form satisfying this requirement would be $M_w = f(M_0) = \gamma M_0$ where γ is a constant. Thus we have,

$$ESR = f(M_0) / M_0 = \gamma \quad (20A)$$

Equations (20) and (20A) provide a physical significance for *ESR*.

Let N be the total number of water absorbing sites in a bead and $\rho_N = N / V_0$ be the number of sites per unit dry volume where, V_0 is the volume of the dry hydrogel. The density of dry hydrogel is $\rho_0 = M_0 / V_0$. The mass of a water molecule is $m = 2.99146 \times 10^{-23}$ gm.

Thus we can write,

$$\rho_N = \frac{N}{V_0} = \frac{(M_{\max} - M_0)/m}{V_0} \quad (21)$$

$$M_{\max} = V_0(\rho_0 + m\rho_N) \quad (22)$$

Thus, the number of such sites per unit mass of dry hydrogel is,

$$\rho_M = \rho_N / \rho_0 = \frac{N/V_0}{M_0/V_0} = \frac{M_{\max} - M_0}{mM_0} \quad \text{or, } M_{\max} = M_0(1 + m\rho_M) \quad (23)$$

$$\text{Thus, } ESR = q_e = \frac{M_{\max} - M_0}{M_0} = m\rho_M \quad (23A)$$

The values of ρ_0 , ρ_N and ρ_M , calculated from experimental data, are shown in TABLE 3.

Sample	A	B	C	D	E	F
ρ_0 ($gm\ cm^{-3}$)	0.622	0.766	2.001	1.382	1.558	1.520
ρ_N (cm^{-3})	3.200×10^{24}	5.830×10^{24}	1.653×10^{25}	7.388×10^{24}	8.034×10^{24}	6.748×10^{24}
ρ_M (gm^{-1})	5.145×10^{24}	7.611×10^{24}	8.261×10^{24}	5.346×10^{24}	5.157×10^{24}	4.439×10^{24}
λ	0.994	0.895	0.844	0.932	0.989	0.948

Theoretical Model:

In the present study we have built up a mathematical model regarding the swelling behaviour of hydrogel, leading to the expression of equation (11), which has been found to be strictly obeyed by our experimental data.

Let η be the number of pores and r be the average radius of them at any instant during the swelling process. Let us also assume that a pore has the shape of a hollow cone having its base on the outer surface of the spherical hydrogel bead. Let κR be the average depth of a pore (i.e. the height of such a hollow cone) where $0 < \kappa \leq 1$ and R is the radius of hydrogel bead. If f be the fraction of surface area covered by pores, we can write,

$$\eta\pi r^2 = f(4\pi R^2) \quad (24)$$

$$\text{Or, } r = \sqrt{\frac{4f}{\eta}} R \quad (24A)$$

Total surface area (A) in contact with water is the sum of areas on the spherical surface and inside these conical pores. Thus we have,

$$A = (1-f)4\pi R^2 + \eta\pi r\sqrt{r^2 + \kappa^2 R^2} \quad (25)$$

Substituting for r in equation (25) from equation (24A) we get,

$$A = \{4(1-f) + \beta\}\pi R^2 \quad (26)$$

$$\text{Where } \beta = \sqrt{4f(\eta\kappa^2 + 4f)} \quad (26A)$$

Let δ be the thickness of active layer on this area (A) exposed to water. This layer, of volume $A\delta$, contains active sites capable of getting attached to water molecules. At any time t , let n be the number of water molecules already attached to the hydrogel and N be the total number of such sites in that piece of hydrogel in dry state. Thus, the dynamics of absorption, by vacant site occupation, may be expressed mathematically by,

$$\begin{aligned} \frac{dn}{dt} &= \text{no. of vacant sites in the region exposed to water at the time } t \\ \text{Or, } \frac{dn}{dt} &= \frac{\text{vol. of active layer}}{\text{vol. of spherical hydrogel}} (\text{total no. of vacant sites at the time } t) \\ \text{Or, } \frac{dn}{dt} &= \frac{3\delta\{4(1-f) + \beta\}}{4R} (N-n) \end{aligned} \quad (27)$$

Since $\eta \gg f$, we can write $\beta = 2\kappa\sqrt{f\eta}$ from equation (26A) for a sufficiently large value of κ . Now, using the equation (24) along with the relation $\beta = 2\kappa\sqrt{f\eta}$ we have,

$$\beta = \frac{4\kappa f R}{r} \quad (28)$$

Substituting equation (28) into (27) we get,

$$\frac{dn}{dt} = 3\delta(1-f)\frac{N-n}{R} + \frac{3\delta \kappa f}{r}(N-n) \quad (29)$$

Instead of considering conical shaped pores, one can also consider the existence of cylindrical pores, each having an average depth of κR and cross section πr^2 . In that case, one gets the following differential equation without any approximation in its mathematical derivation.

$$\frac{dn}{dt} = 3\delta(1-f)\frac{N-n}{R} + \frac{6\delta \kappa f}{r}(N-n) \quad (29A)$$

The equations (29) and (29A) have the same form, except for a constant in the second term on the right hand side of the equations.

From micrographs of highly porous hydrogels, provided by various groups of researchers [28, 29], it is often found that almost the entire surface area of hydrogel is covered with pores, making f very close to unity. Taking $f \approx 1$, we may neglect the first term on the right hand side of equations (29, 29A) and its new form would be,

$$\frac{dn}{dt} = \frac{C\delta\kappa}{r}(N-n) \quad (30)$$

Where $C = 3,6$ for conic and cylindrical pores respectively.

Assuming δ, κ, r to be constant and considering the boundary condition that, $n = 0$ at $t = 0$, the solution of the above differential equation is,

$$n = N(1 - e^{-t/\tau}) \quad (31)$$

$$\text{Where, } \tau \propto \frac{r}{\delta\kappa} \quad (32)$$

Equation (32) is an important derivation of our theoretical model which shows that, smaller the value of the ratio $r/\delta\kappa$ for a hydrogel, faster would be its progress towards the saturation in water absorption.

After absorbing n molecules of water, the mass of hydrogel becomes,

$$M = M_0 + nm = M_0 + mN(1 - e^{-t/\tau}) \quad (33)$$

Where m is the mass of a water molecule, $m = 2.99146 \times 10^{-23}$ gm.

From equation (33) we have, at $t \rightarrow \infty, M \rightarrow M_{\max} \equiv M_0 + mN$. Thus we can write,

$$M - M_0 = (M_{\max} - M_0)(1 - e^{-t/\tau}) \quad (34)$$

Equation (34) is the expression which is identical to that of equation (11) which is found to be strictly obeyed by all our hydrogel samples, as evident from Figure 1.

The fractional volume of pores (P) of hydrogel can be calculated from this formulation. It is defined as,

$$P = \frac{\text{pore volume}}{\text{total volume}} = \frac{\eta \left(\frac{1}{3} \pi r^2 \kappa R \right)}{\frac{4}{3} \pi R^3} = \frac{\eta \kappa r^2}{4R^2} \quad (35)$$

Substituting from equation (24) into equation (35) we get,

$$P = \kappa f \quad (36)$$

Equation (36) shows an important finding of this model, describing the fact that the porosity of hydrogel is proportional to the fraction of outer surface area occupied by pores. According to equation (32), τ varies inversely as κ , which is proportional to P as per equation (36). Thus, larger values of P drive the process faster towards saturation. Using equation (36), the second term on the right side of equation (29) becomes $3\delta P(N-n)/r$. Taking f to be very close to unity in equation (29), we have arrived at equation (34) which has a perfect agreement with our experimental data.

Let us define a quantity λ , denoting the ratio of overall increase in volume of the bead to the total volume of water molecules absorbed by the hydrogel. Thus, the volume of hydrogel, at any time t , is given by,

$$V(t) = V_0 + \frac{\lambda m}{\rho_w} n(t) = V_0 + \frac{\lambda m}{\rho_w} N(1 - e^{-t/\tau}) \quad (37)$$

Here m and ρ_w are respectively the mass of a water molecule ($m = 2.99146 \times 10^{-23} \text{ gm}$) and density of water. At $t \rightarrow \infty$, we have, $V(t) \rightarrow V_{\max} = V_0 + \frac{\lambda m}{\rho_w} N$. Thus, equation (37) may be expressed as,

$$V(t) - V_0 = (V_{\max} - V_0)(1 - e^{-t/\tau}) \quad (38)$$

Using the relation $N = \rho_N V_0$, equation (37) can be expressed as,

$$V(t) = V_0 \left[1 + \lambda m \frac{\rho_N}{\rho_w} (1 - e^{-t/\tau}) \right] \quad (39)$$

Using the relation $N = \rho_M M_0$, equation (33) can be expressed as,

$$M(t) = M_0 \left[1 + m \rho_M (1 - e^{-t/\tau}) \right] \quad (40)$$

In the above equations (39, 40), the time dependence of mass and volume of a swelling hydrogel has been expressed in terms of their initial values and some intrinsic properties of the material. From these equations, the relation between volume change and mass change can be expressed as,

$$V(t) - V_0 = \frac{\lambda}{\rho_w} [M(t) - M_0] \quad (41)$$

The values of λ , obtained by fitting equation (39) to our experimental data, are listed in TABLE 3. This numerical curve fitting is shown in Figure 3 which shows that our formulation agrees very well with experimental observations. The values of τ used for this curve fitting are the same as listed TABLE 1. The values of λ are close to unity, implying the fact that the increase in volume of hydrogel, by absorption of a given amount (mass) of water, is very close to the volume of water having the same mass. This fact is described by equation (41) mathematically. Figure 4 shows that most of the data points are lying very close to the straight line corresponding to $\lambda = 1$, in accordance with equation (41).

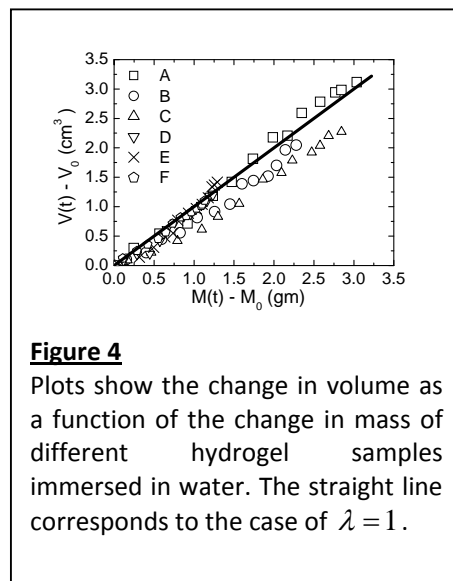
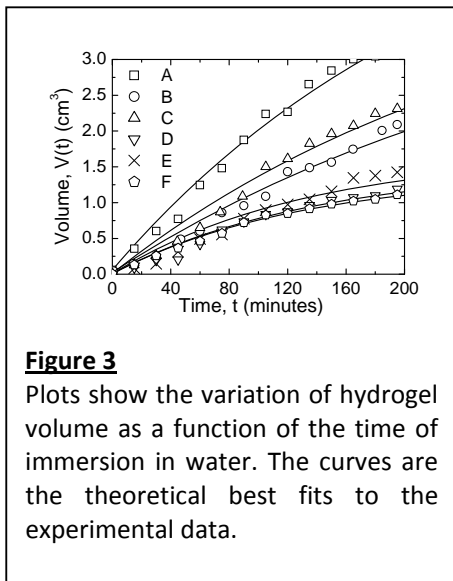
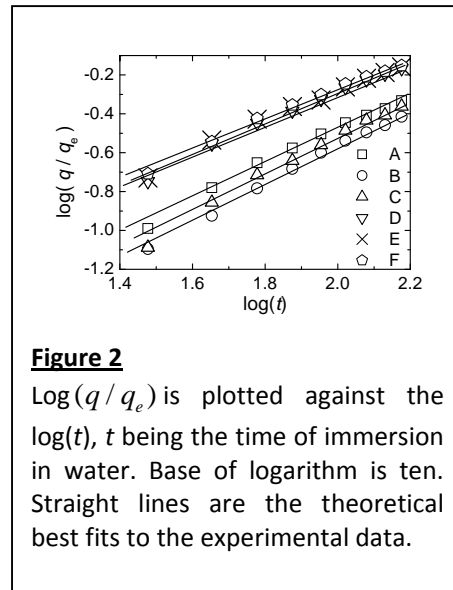
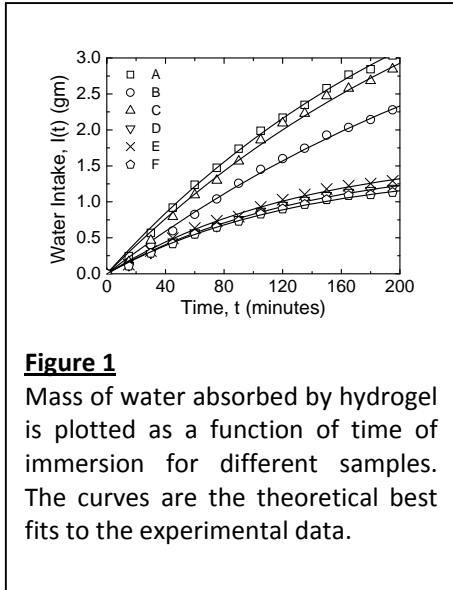
Using equations (33) and (44), rise in volume for the absorption of a single water molecule is given as,

$$\frac{V(t) - V_0}{n(t)} = \frac{V(t) - V_0}{[M(t) - M_0] / m} = \frac{m\lambda}{\rho_w} \quad (42)$$

Thus, it is found to be a constant quantity for our samples, independent of time, mass and volume. For all practical purposes one can take $\rho_w = 1\text{gm/cc}$.

Conclusions:

The present theoretical model has been developed assuming conical or cylindrical shape of the pores. This is an ideal case which is different from the real situation where pores of various sizes and shapes are present in the hydrogel. The model can be improved by considering a suitable statistical distribution of sizes and shapes of the pores. The applicability of this model would be wider if one solves equation (27) without any approximation. To verify the predictions of such models experimentally, one must measure both mass and volume of swelling hydrogel with as much precision as possible. In the present study mass measurement has greater accuracy than that of volume measurement, owing mainly to the deviations from spherical shape. The unique feature of this study is that, on the basis of a completely new concept, based on the phenomenon of occupying vacant polymer sites by water molecules, the mechanisms of mass rise and volume expansion have been rigorously explained and it has also been shown that larger porosity induces faster absorption of water by hydrogels.



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