Study of the swelling behavior of Spherical water-gels in Sugar Solution

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Abstract

In the present study a simple experiment has been performed with the most commonly used and widely available spherical water-gel crystals in the shape of beads. Immersing the beads in sugar solution of variable concentrations the mass of the swallowed beads were measured at regular time intervals. The experimental results so obtained have been explained using an analytical approach. A theoretical model has been developed based on the consideration of water absorption through vacant polymer sites in a highly porous hydro-gel. Considerations of cylindrical and spherical pores in this model predicted almost the same swelling behavior. It has been shown that the characteristic time of growth of the hydro-gels is linearly related with the sugar concentration. Some references have been cited which agree well with the results found in this experiment, thus validating the assumptions made in the analytical model used.

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INTRODUCTION

Hydro-gel polymers commonly available in the market under various names such as magic pearl jelly, water-gel or crystal soil etc. are often used as decorative as well as source of water for indoor flower pots, vases etc. These super-absorbent gels are of various chemical compositions but having almost the same swelling behavior. They have the capability to absorb water at a very fast rate and grow to a maximum of 150-300 times their weight in the process. The swelling properties of water-gels are

mainly related to the elasticity of the polymer network, the presence of hydrophilic functional groups in the polymer chains, the extent of cross-linking, and porosity of the polymer [1]. Under dry conditions they de-swell very slowly. Their water retentive property finds a number of applications in the industry. These gels are used as moisture retaining soil additives in gardening; they also absorb liquid fertilizer just as they do water and serve as food reservoirs in the soil for plants. Hydro-gels have several major medical uses including tissue engineering, wound dressing and controlled drug release in their swollen state [2, 3]. Disposable nappies are made making use of the ability of hydro-gels to take up and retain water. They are also used to make soft contact lenses. The swelling and de-swelling behavior of hydro-gels is used to detect certain analytes such as volatile organic compounds [4, 5], various gases [6, 7], biological molecules [8, 9, 10] etc. Hydro-gels 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 [5]. The sensitivity of hydro-gels 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 [11]. Miniaturized hydro-gel objects are strong candidates for sensors and actuators in micro-electro-mechanical systems (MEMS) technology [12]. Electro-responsive ionic polymer gels have been employed for designing dust wipers, miniature robotic arms etc [13].

Scientists still do not fully understand why and how hydro-gels manage to absorb so much water and there is still plenty of ongoing research into their properties and uses. Understanding their structure helps to explain their properties which in turn is used to design new hydro-gels to perform new functions.

MATERIAL AND METHOD

In the present study instead of using the standard theories of diffusion, we have described absorption of water in sugar solution in terms of the phenomenon of attachment of ionized water molecules to charged sites on the polymer chains and thereby causing a mass growth of hydro-gel.

Spherical white hydro-gel beads of most abundantly found and widely used in Kolkata were obtained from a standard source. The main ingredients of these gels are poly-acrylate or poly-acrylamide. They are a type of superabsorbent polymers 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 [14, 15].

These spherical hydrogel beads (white in color and almost identical in size) were kept immersed in sugar solution of a certain concentration and the mass of each bead were measured at intervals of 15 *minutes*. Each time, after taking out from water, a bead was put in contact with blotting paper for removing excess water from its surface and the mass was measured by a digital weighing machine having an accuracy of 0.001 *gm*. Stop watches, having an accuracy of 0.2 second, were used for time measurement. The concentration of the sugar solution was now increased and the experiment was repeated. In these ways we have varied the sugar concentration from 0 % to 25 % with a step of 5 %.

Theoretical Modeling

A mathematical model has been developed regarding the swelling behavior of the beads [16], which has been found to strictly obey the experimental data.

Hydro-gels are highly porous and the pores are distributed all over its surface area. Let η be the number of pores and r be their mean radius at any

instant of time 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 hydro-gel bead. We also assume that 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 hydro-gel bead. If f be the fraction of surface area covered by pores, we may write

$$r = \sqrt{\frac{4f}{\eta}} \, R \qquad (3.1)$$

Total surface area (A) in contact with water is the sum of areas on the spherical surface and insides of these conical pores. Thus we have [16]

$$A = \left[4(1-f) + \beta \right] \pi R^2, \qquad (3.2)$$

with $\beta = \sqrt{4f(\eta \kappa^2 + 4f)}$. Let δ be the thickness of active layer on this area (A) exposed to sugar solution. 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 hydro-gel and N be the total number of such sites in that piece of hydro-gel in dry state. Thus, the dynamics of absorption, by vacant site occupation, may be expressed mathematically by [16] (as according to our earlier assumption the rate of variation of n being equal to the number of vacant sites in the region exposed to water at time t

$$\frac{dn}{dt} = \frac{3\delta \left[4(1-f) + \beta \right]}{4R} (N-n) \qquad (3.3)$$

Since $\eta \quad f$, for a sufficiently large value of κ we may write $\beta = 2\kappa\sqrt{f\eta}$, which following "(3.1)" leads to

$$\beta = \frac{4\kappa f R}{r} \qquad (3.4)$$

Hence (with p=3)

$$\frac{dn}{dt} = 3\delta(1-f)\frac{N-n}{R} + \frac{p\delta \, \kappa f}{r}(N-n) \qquad (3.5)$$

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, which leads to $p=6$ in "(3.5)". From micrographs of highly porous hydro-gels, provided by various groups of researchers [17, 18], it is often found that almost the entire surface area of hydro-gel 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 "(3.5)" and its new form would be

$$\frac{dn}{dt} = \frac{C\delta \, \kappa f}{r}(N-n) = \frac{1}{\tau}(N-n) \qquad (3.6)$$

Here τ is the time constant or characteristic time for the process of swelling of hydro-gel in pure water.

Now to formulate the swelling behavior in sugar solution we consider that in sugar solution, a large number of water molecules are bound to sugar molecules and are thus unavailable for attachment at the active sites of the hydro-gel. Hence the probability of attachment of water molecules to active sites may be expected to depend upon the fraction of water molecules not hindered in any way to get attached to active sites of water-gel. For larger concentrations of sugar, this fraction will be smaller and consequently, the chance of attachment becomes smaller. The modified form of equation "(3.6)" may be expressed as

$$\frac{dn}{dt} = \frac{K}{\tau}(N-n), \, (0 < K \leq 1) \qquad (3.7)$$

The parameter K denotes the fraction of water molecules capable of interaction with active sites of gel which may be defined in the following way.

$$K = \frac{N_w - N_2}{N_w} = 1 - \frac{N_2}{N_w} \qquad (3.8)$$

where, N_w is the number of water molecules present per unit volume of water. This is actually the number of water molecules per unit volume, which are all equally capable of interaction with active sites when the hydro-gel bead is immersed in pure water. N_2 is the number of water molecules which are prevented from having interaction with active sites, per unit volume, in a sugar solution of a certain concentration

(say P% strength, i.e. P *gm* of sugar per 100 *cc* of water).

Experimental Results

It was our experimental observation that the mass of 10 *cc* of 15% sugar solution is 10.626 *gm*. We know that 10cc of 15% solution contains 1.5 *gm* of sugar. Therefore, this solution contains (10.626-1.5) *gm* = 9.126 *gm* of water whose volume is nearly 9.126 *cc*. Hence the volume occupied by sugar in this solution is $(10 - 9.126) c.c. = 0.874$ *cc*. Number of sugar molecules in 1.5 *gm* of sugar being $(1.5/342) \times 6.023 \times 10^{23} = 2.641 \times 10^{21}$ (as the molecular weight of sugar $C_{12}H_{22}O_{11}$ is $M_S = 342$). Therefore the volume occupied by each sugar molecule is, say, $v_S = 0.874/(2.641 \times 10^{21}) cc = 3.309 \times 10^{-22} cc$. The volume of one water molecule is $v_w = M_w/(\rho_w N_A) = 2.989 \times 10^{-23} cc$, N_A being the Avogadro number. Here, the molecular weight of water is $M_w = 18$ with density ρ_w 1 $gm.cc^{-1}$.

Now for 1 *cc* of solution one may write

$$N_s v_s + N_w v_w = 1 \qquad (4.1)$$

Where N_s, N_w are respectively the numbers of sugar molecules and water molecules per cc in a solution of a certain concentration (say P%). Thus from the above equation we have

$$N_w = \frac{1 - N_s v_s}{v_w} = \frac{1}{v_w}\left(1 - v_s \frac{P N_A}{100 M_S}\right) = \frac{1}{v_w}\left(1 - 5.826 \times 10^{-3} P\right)$$

$$(4.2)$$

For smaller values of P we obtain

$$N_w \quad \frac{1}{v_w} = \frac{\rho_w N_A}{M_w} = \frac{1 \times 6.022 \times 10^{23}}{18} = 3.346 \times 10^{22}.$$

Now the number of sugar molecules, per unit volume, in a solution of P% concentration is given by

$$N_s = \frac{(P/100) N_A}{M_S} \qquad (4.3)$$

Let C_1 be the average number of water molecules hindered by each sugar molecule, in different possible ways, in the solution. Hence we have

$$N_2 = C_1 N_s = C_1 \frac{(P/100) N_A}{M_S} \qquad (4.4)$$

Hence following "(3.8)" we obtain

$$K = 1 - \alpha P , [\alpha = \frac{C_1 M_W}{100 \rho_w M_S}]. \qquad (4.5)$$

Now using "(4.5)" in "(3.7)" we get

$$\frac{dn}{dt} = \frac{(1 - \alpha P)}{\tau}(N - n) = \frac{1}{T}(N - n). \qquad (4.6)$$

with

$$T = \frac{\tau}{1 - \alpha P} \qquad (4.7)$$

Here, T is the new time constant, characteristic of the swelling process of hydro-gel in a solution of strength P%.

For pure water $P = 0$ and we have $K = 1$ and $T = \tau$. Then "(4.6)" reduces to "(3.6)" which has already been solved to derive the mass versus time relation for the hydro-gel swelling process in pure water [16]. Modifying this mass-time relation accordingly (using "(4.6)") we get

$$M = M_0 + nm = M_0 + mN(1 - e^{-t/T}) \qquad (4.8)$$

Where M_0 is the initial mass or dry mass, n is the number of water molecules attached to the active sites of the hydro-gel and m is the mass of a water molecule, $m = 2.99146 \times 10^{-23} gm$. Equation "(4.8)" may also be expressed as

$$M = M_0 + mM_0\rho_M(1 - e^{-t/T}) = M_0\left[1 + m\rho_M(1 - e^{-t/T})\right]$$

$$(4.9)$$

Here, $\rho_M = N/M_0$ has been calculated for different samples of hydro-gel.

By a rearrangement of terms and using the relation "(4.7)", "(4.8)" may be expressed as

$$\tau \ln\left[1 - \frac{1}{m\rho_M}\left(\frac{M}{M_0} - 1\right)\right]^{-1} = (1 - \alpha P) \ t = K t \qquad (4.10)$$

Equation "(4.10)" suggests that if its left hand side is plotted as a function of t, it will be a straight line passing through the origin. The slope of this line is K.

Fitting our experimental data numerically to "(4.8)", we have determined the values of T for different concentrations of sugar solutions (figure 1). These values are listed in table 1.

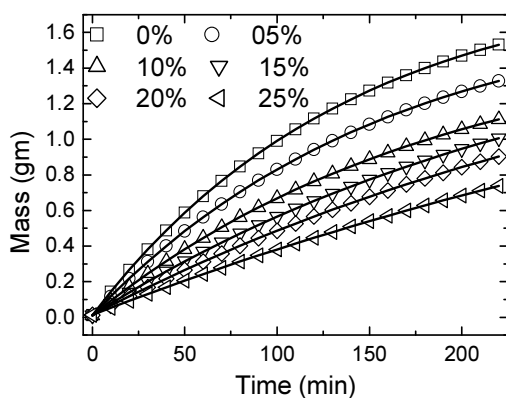| Table 1				
Strength of sugar solution	M_0 (in gm) (By direct measurement)	N (by curve fitting)	T (min) (by curve fitting)	$\rho_M = N/M_0$ (1/gm)
0%	0.012	6.410×10^{22}	140.175	5.342×10^{24}
05%	0.011	5.883×10^{22}	159.387	5.348×10^{24}
10%	0.010	5.341×10^{22}	188.333	5.341×10^{24}
15%	0.011	5.890×10^{22}	263.811	5.355×10^{24}
20%	0.012	6.427×10^{22}	352.293	5.357×10^{24}
25%	0.013	6.961×10^{22}	512.824	5.351×10^{24}

According to "(4.7)"

Figure 1
Mass of hydro-gel is plotted as a function of time of immersion in different concentrations of sugar solutions. The curves are the theoretical best fits to the experimental data. The fitting gives us the values of N and T.

Now from "(4.5)" and using the value of α obtained from the experimental study of the sample we get

$$C_1 = \frac{100 \rho_w M_S \alpha}{M_w} = \frac{100 \times 1 \times 342 \times \alpha}{18} = 1900\alpha = 1900(2.977 \times 10^{-2}) = 56.563$$

$$(4.12)$$

Hence, the average number of water molecules (N_1) not free to get attached to active sites in 1cc of solution of strength P% is

$$\frac{1}{T} = \frac{1 - \alpha P}{\tau} = \frac{1}{\tau} - \frac{\alpha}{\tau} P \qquad (4.11)$$

According to our theoretical formulation (as described by "(4.11)" above), a plot of $1/T$ versus P will be a straight line with a negative slope ($-\alpha/\tau$) and the corresponding intercept is $1/\tau$. Figure 2 shows a plot of $1/T$ as a function of concentration (P) for our sample regarding the swelling of hydro-gel in sugar solution. This plot is in very good agreement with "(4.11)". The slope and intercept of the best fitting straight line are -2.155×10^{-4} and 7.240×10^{-3} respectively. The value of τ for the sample is 138.122 minutes, which should ideally be the value of T for $P = 0$. The value we have from the table 1 is $\alpha/\tau = 2.155 \times 10^{-4}$ and hence we obtain $\alpha = 2.977 \times 10^{-2}$.
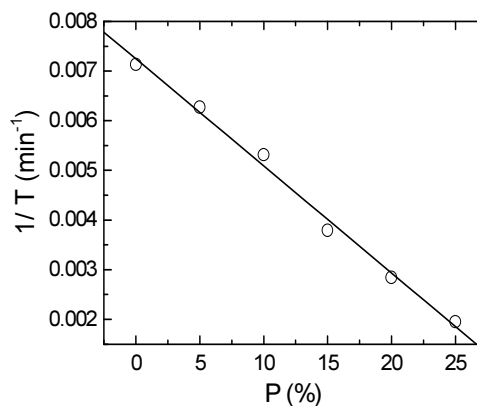

Figure 2
The reciprocal of time constant T has been plotted as a function of concentration percentage of sugar solution in which hydro-gel was immersed.

$$N_1 = C_1 N_s = C_1 \frac{(P/100) N_A}{M_S} = \left(9.960 \times 10^{20}\right) P \qquad (4.13)$$

And the fraction of free water molecules in a solution of strength P% is

$$f = \frac{N_1}{N_w} = \frac{\left(9.960 \times 10^{20}\right) P}{3.346 \times 10^{22}} = \left(2.977 \times 10^{-2}\right) P \qquad (4.14)$$

Concluding Remarks

The present model has been developed with the assumption of 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 hydro-gel. The model may be improved by considering a suitable statistical distribution of sizes and shapes of the pores. 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 has been rigorously studied.

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