

## The effect of chain stiffness on moisture diffusion in polymer hydrogel by applying obstruction-scaling model

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In order to understand the moisture diffusion, we combine the obstruction-scaling model with the moisture clustering in confined spaces of the polymer hydrogel, with relevance to the performance of the super desiccant polymer. Special attention is focused on elucidating the effect of chain stiffness by considering the conformation of polymer chain on the basis of polymer physics. Relevant parameters for calculations are determined from literature information as well as the best fits for reported data performed with the copolymer. Our results exhibit the moisture diffusion decreases with increasing chain stiffness represented by the persistence length. Note that the larger persistence length provides smaller radius of openings in void spaces, resulting in the stronger hindrance effect on the moisture diffusion. Higher temperature makes the water molecules to be easier to form clusters, which provides the decrease in diffusivity. The increase of moisture diffusion at low humidity is attributed to the swelling of the chain, whereas its decrease at high humidity results from the water clustering.

**Keywords:** chain stiffness, polymer hydrogel, moisture diffusion, water cluster, obstruction model

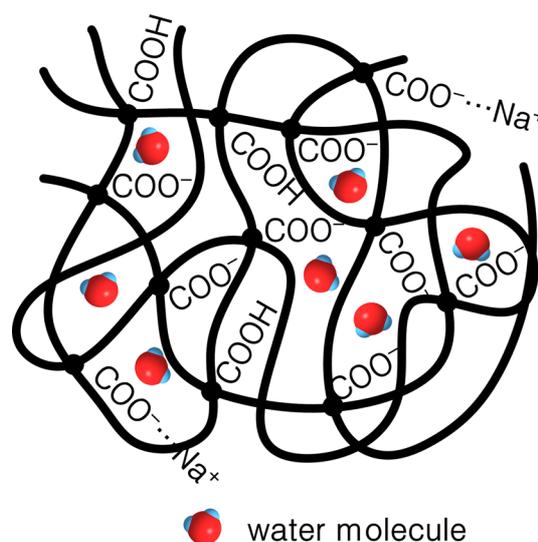
### Introduction

As an issue of dehumidification for living space, super desiccant polymer (SDP) draws attention to be one of the promising desiccant materials. Desiccation phenomena contain more complicated mechanisms, which requests efforts to examine the transport of water molecules and the physics of the polymer chain. In order to develop the high efficient SDP, one needs to understand the moisture diffusion in polymer hydrogel, as shown in Fig. 1.

A number of models have been proposed to explain the movement of solute molecule in homogeneous hydrogels. Complementing the free volume theory, the hydrodynamic-scaling model reported by Cukier (1984) presented a more consistent result. Then, the steric factor was incorporated into discussions for the hindered diffusion (Koch and Brady 1986) and the diffusivity was found to decrease with increasing ratio of the solute radius to the fiber radius (Phillips *et al.*, 1990). It has also been reported that the solute diffusivity is affected by the stiffness of the polymer chains, with solute diffusion being greater in gels having thicker polymer chains (Clague and Phillips, 1996).

Ogston *et al.* (1973) assumed that solute diffusion in the hydrogel occurs by a succession of directionally random unit steps, and that the unit step does not take place if the solute encounters a polymer chain. Underlying this principle, the obstruction-scaling model was developed by

Amsden (1999) taking the size of solute molecule into consideration. Subsequently, scaling relationship was incorporated into an obstruction-based model and shown to account for the effects of ionization degree and chain stiffness (Amsden *et al.*, 2002). Quantifying the effects of the hydrodynamics and the obstruction, the degree of ionization and the Flory-Huggins interaction between polymer and solvent are important to predict the experimental results in ionic and non-ionic polymers, respectively.



**Fig. 1.** (Color online) Schematic of water molecules in charged polymer hydrogel.

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There are many sorption models that describe moisture content (cf., sorption capacity) in fibrous desiccant materials as a function of the water activity (or relative humidity), on the basis of the curve fittings to the experimental data as well as the multilayer theory (Peleg, 1993; Timmermann 2003; Park, 1986). Among them, Park model provides a more useful prediction in the wider range of water activity because it gives a physical approach to elucidate three phenomena independently affecting the moisture sorption to fibers. In this work, the obstruction-scaling model is combined with the moisture clustering in the polymer hydrogel to serve as a basis for understanding the moisture diffusion, having relevance in the performance of the SDP. We especially elucidate the effect of chain stiffness by considering the conformation of polymer chain. The parameters for sorption model are obtained from the reported data performed by sorption-desorption tests with the copolymer based SDP.

### Model Developments

The model starts with the idea of physical obstruction and the distribution of opening radii within the hydrogel expressed using the equation derived by Ogston (1958). This distribution is converted to fibers of finite thickness by incorporating the radius of the polymer chain, and then the diffusivity in the hydrogel  $D_g$  can be expressed as

$$\frac{D_g}{D_0} = \exp\left[-\frac{\pi}{4}\left(\frac{r_s+r_f}{r_{ov}+r_f}\right)^2\right]. \quad (1)$$

Here,  $D_0$  is the self-diffusivity of diffusate (cf., water molecule or moisture in this study),  $r_s$  is its hydrodynamic radius, and  $r_f$  is the polymer chain radius. Note that  $r_f = (M_w/l_m\pi\rho_p N_A)^{1/2}$ , where  $l_m$  is the length of monomer unit (nm),  $M_w$  is the molecular weight of monomer (g/mol),  $N_A$  is the Avogadro's number, and  $\rho_p$  is the density of the polymer. For ionic polymers, the average radius of the openings between polymer chains is given as (Skouri *et al.*, 1995; Amsden *et al.*, 2002)

$$r_{ov} = \frac{k_s}{2}(\phi l)^{-1/2}(\alpha C_\infty)^{-1/4} \quad (2)$$

where  $k_s$  is the constant of proportionality and  $l$  is the equivalent average bond length of a monomer (nm). The polymer volume fraction in gel  $\phi$  is obtained dividing the net volume of polymer by the total volume (consisting of polymer + moisture + pore), which can be described as a function of sorption capacity  $M$  in terms of  $\phi = 1 - (1 + \rho/M)^{-1}$ . The degree of ionization  $\alpha$  is obtained by finding the root of the equation given as  $\text{pH} = \text{p}K_a - 2\log[\alpha/(1-\alpha)]$  with the acid dissociation constant  $K_a$ .

According to random-walk statistics of the freely jointed polymer chain, the unperturbed mean square end-to-end distance can be expressed as  $\langle R_E^2 \rangle_o = nb_n^2$ , where  $n$  is the

number of backbone bonds composing the chain and  $b_n$  is the length of an effective random-walk step.  $\langle R_E^2 \rangle_o$  separates one end of the molecule from the other at the theta state. Because bond angle restrictions make the average coil size  $\langle R_E^2 \rangle_o$  more expanded than would otherwise be the case,  $b_n$  is larger than the average bond length  $l$ . Thus, one can obtain the characteristic ratio of the polymer chain  $C_\infty$ , given by

$$C_\infty = \frac{\langle R_E^2 \rangle_o}{nl^2} = \frac{b_n^2}{l^2}. \quad (3)$$

If the degree of polymerization  $N$  is used instead of  $n$ , one can define the statistical segment length  $b$ , as  $\langle R_E^2 \rangle_o = Nb^2$ . Further, if a fully extended length (or contour length)  $L$  of the chain is applied, then another effective step size (namely persistence length)  $l_p$  is defined as  $\langle R_E^2 \rangle_o = L(2l_p)$ , where  $2l_p$  corresponds to the Kuhn length. Note that one has  $l_p = (C_\infty/1.64)l$ , since  $L \approx 0.82nl$  for ordinary flexible synthetic polymers (Larson, 1999). For the stiffer and extended polymer chain, the value of  $C_\infty$  becomes higher, where  $C_\infty$  can be evaluated from the relationship using Flory theory.

The sorption capacity  $M$  is defined as the ratio of the net water mass gained to the mass of dry polymer at the equilibrium. Park model has been a good predictor of the sorption capacity by the relative humidity of air  $a_w$ , given as

$$M = \frac{A_L\beta_L a_w}{1 + \beta_L a_w} + k_H a_w + K_C a_w^n \quad (4)$$

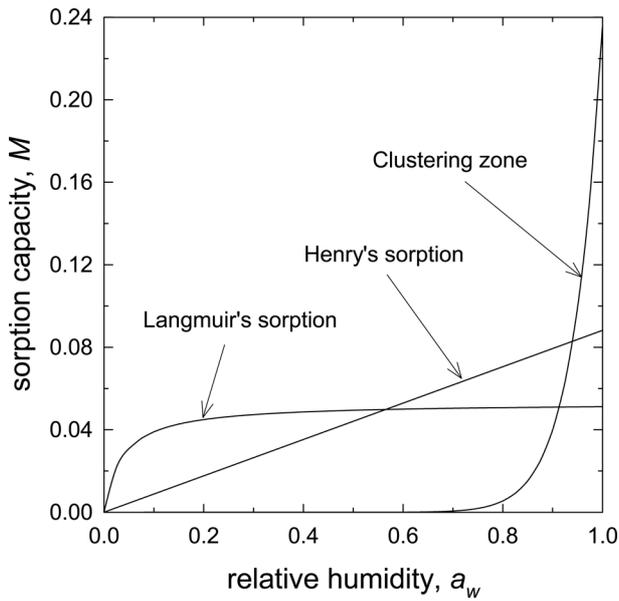
where  $A_L$  is the Langmuir capacity constant,  $\beta_L$  is the Langmuir affinity constant,  $k_H$  is the solubility coefficient of Henry's type,  $K_C$  is the equilibrium constant for the clustering, and  $n$  is the mean number of water molecules per cluster. Schematic presentation of the moisture sorption described by Park model is shown in Fig. 2. In a low water activity, the adsorption rules out the kinetics so that moisture content increases sharply as the activity does, so-called the Langmuir region. In an intermediate level of the activity, moisture content is directly proportional to the activity, that is to say, the Henry's law region. Above a certain activity, usually around 0.8, moisture content rises sharply again, and we call it as the cluster region.

Applying Eq. (4) into the definition of mean cluster size investigated by Starkweather (1963) results in the mean cluster size of water molecule based on the Park model  $S_{Park}$  (Gouanve *et al.*, 2007) such that

$$S_{Park} = \frac{\rho^2}{M^3(1+(\rho/M))^2} \left[ \frac{A_L a_w}{(1+\beta_L a_w)^2} + k_H a_w + K_C n a_w^n \right]. \quad (5)$$

$S_{Park}$  identifies the average number of molecules in the vicinity of one water molecule, and  $\rho$  is the ratio of the density of the water  $\rho_s$  to the density of the polymer  $\rho_p$ .

Prior to water cluster formations,  $r_s$  can be calculated by Stokes-Einstein equation as  $r_s = k_B T / 6\pi\eta D_0$ . Here,  $k_B$  is



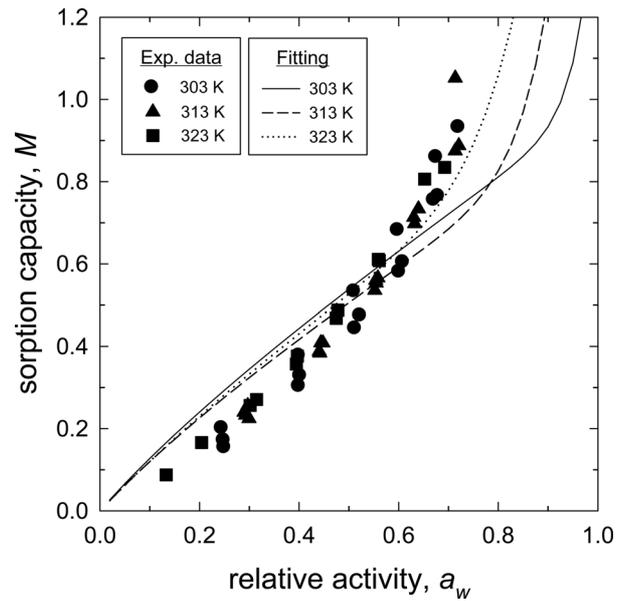
**Fig. 2.** Mechanisms of water sorption in polymer hydrogel according to Park model for hypothetical values of  $A_L = 0.053$ ,  $\beta_L = 27.81$ ,  $k_H = 0.088$ ,  $K_C = 0.236$ , and  $n = 16.87$ .

the Boltzmann constant (J/K),  $T$  is the absolute temperature (K),  $\eta$  is the dynamic viscosity of water. Once clusters are formed,  $r_s$  should be altered accordingly. We suggest  $r_s$  modified with the geometric factor  $\sigma$  such that  $r_s = (k_B T / 6\pi\eta D_0) \exp(\sigma S_{Park})$ . Then, Eq. (1) leads to

$$\frac{D_g}{D_0} = \exp \left[ -\pi \left( \frac{(k_B T / 6\pi\eta D_0) \exp(\sigma S_{Park}) + r_f}{k_s(\phi l)^{-1/2} (\alpha C_\infty)^{-1/4} + 2r_f} \right)^2 \right]. \quad (6)$$

## Results and Conclusions

Fig. 3 presents the best fits of sorption capacity  $M$  as a function of relative humidity  $a_w$  by applying the least-square regression for Eq. (4) at different temperatures. Experimental data was taken from literature (Lee and Lee, 2012), where the moisture sorption was measured for the material of poly(acrylamide-co-sodium acrylate). While  $M$  does not depend on the temperature for  $a_w \leq 0.5$ ,  $M$  increases with increasing temperature for  $a_w > 0.6$ . High temperature provides an increase in kinetic energy of molecules, therefore, the temperature increasing allows water molecules to be closer so that it is available to fill with much more water molecules in the same void space of hydrogel. Table 1 summarizes the parameters of Park model used for fitting water sorption with different temperatures. The effect of water clustering on the diffusion is complicated. The water molecules begin forming clusters when  $a_w$  becomes high enough to interact with each other, possibly resulting in the increase of moisture diffusion due to an expansion of the polymer chain network. Simulta-



**Fig. 3.** Experimental data of sorption capacity  $M$  with different relative humidity  $a_w$  and their curve fitting by Park model for various temperatures.

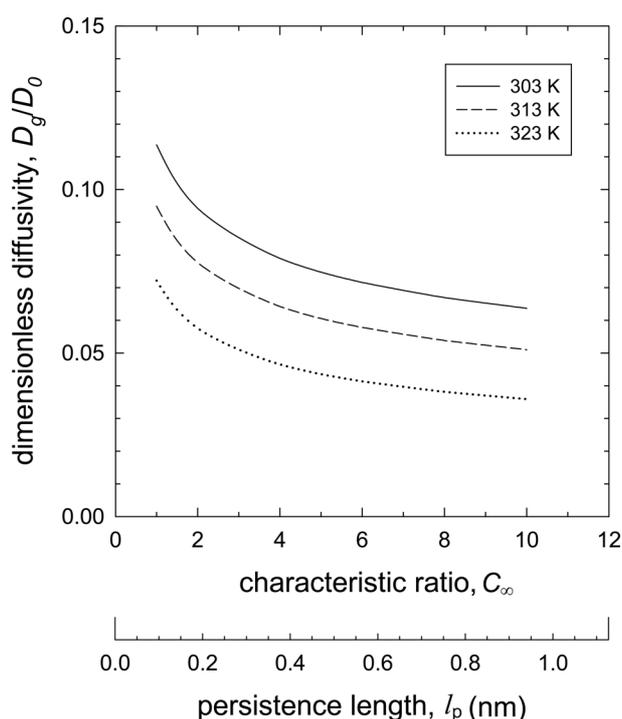
**Table 1.** Parameters of Park model used for fitting water sorption with different temperatures

Temperature (K)	Langmuir		Henry	Water clustering	
	$A_L$	$\beta_L$	$k_H$	$K_C$	$n$
303	0.256	2.226	0.808	0.574	26.310
313	0.266	2.063	0.741	1.933	15.163
323	0.341	1.506	0.755	2.288	9.611

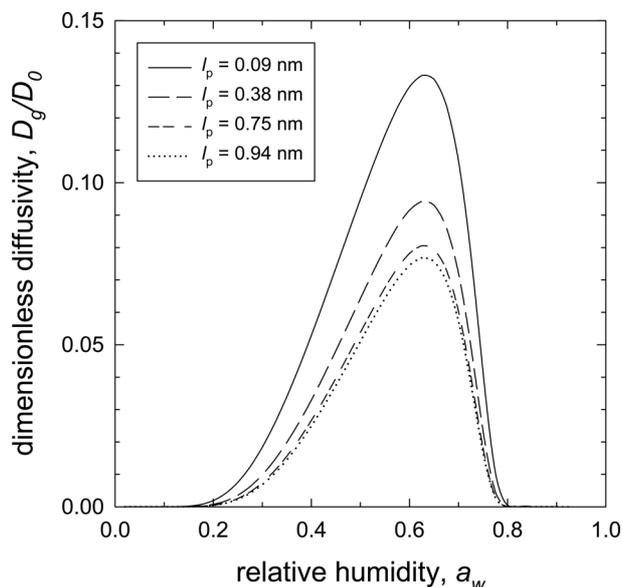
neously, water clustering is accompanied with the decline of diffusivity according to the immobilization of water molecules at high relative humidity (Amsden *et al.*, 2002).

The mean cluster size  $S_{Park}$  can be calculated by using parameters given in Table 1 and Eq. (5) with  $\rho_p = 1.35 \text{ g/cm}^3$  (Okay and Sariisik, 2000).  $S_{Park}$  is required to estimate the moisture diffusivity by Eq. (6). By considering literature information, relevant parameters to apply Eq. (6) are chosen as follows:  $\alpha = 0.8$ ,  $\sigma = 4.25$ , and  $k_s = 2.14 \text{ \AA}^{-1.5}$  for all temperatures. For 303, 313, and 323 K,  $\eta = 7.97 \times 10^{-4}$ ,  $6.53 \times 10^{-4}$ , and  $5.47 \times 10^{-4} \text{ Pa}\cdot\text{s}$ , respectively (Dean, 1999), and accordingly  $D_0$  is estimated as  $2.594 \times 10^{-9}$ ,  $3.238 \times 10^{-9}$ , and  $3.956 \times 10^{-9} \text{ m}^2/\text{s}$ . A reasonable assumption has been employed to the values of  $l$  and  $l_m$  for the copolymer material cited in Fig. 3, because direct measurements of those values are beyond the scope. In view of  $l$  as the bond length of carbon-carbon atoms, we take here  $l = 0.154 \text{ nm}$  and  $l_m = 0.251 \text{ nm}$  from the known values in case of poly(acrylamide). Then,  $r_f$  becomes  $0.34 \text{ nm}$ .

The characteristic ratio  $C_\infty$  is 1 for a freely jointed chain. However, for real chains, bond angle restrictions



**Fig. 4.** Dimensionless moisture diffusivity as a function of characteristic ratio  $C_\infty$  (i.e., persistence length or half of Kuhn length) for various temperatures at  $a_w = 0.5$ .



**Fig. 5.** Dimensionless moisture diffusivity versus relative humidity with different persistence lengths for chain stiffness at 313 K.

lead to values of  $C_\infty$  in the range 4-10. Higher values of  $C_\infty$  correspond to the higher stiffness (Brandrup *et al.*, 2004). Although  $C_\infty$ s of pure poly(acrylamide) and poly(vinyl alcohol) are reported as 8.5 and 8.3, respectively (Bohdanecky *et al.*, 1983; Gudeman and Peppas,

1995), those values for copolymer can change depending on the ratio of each component. Fig. 4 shows the estimated results of dimensionless moisture diffusivity in hydrogel as a function of the characteristic ratio  $C_\infty$  for different temperatures. As described before,  $C_\infty$  is proportional to the persistence length, representing the chain stiffness in polymer hydrogel. It should be emphasized that the dimensionless diffusivity  $D_g/D_0$  decreases with increasing chain stiffness, exhibiting the power scaling as  $D_g/D_0 \sim C_\infty^\nu$  (or  $\sim l_p^\nu$ ) with the slope  $\nu$  as -0.252, -0.270, and -0.303 for 303, 313, and 323 K, respectively. According to Eq. (2),  $C_\infty$  is inversely proportional to the radius of openings  $r_{ov}$  so that higher  $C_\infty$  provides smaller  $r_{ov}$ , resulting in the stronger hindrance effect on the diffusion in hydrogel. The dimensionless diffusivity evidently decreases with increasing temperature, which results from the enhanced formation of water cluster due to higher activity of water molecules at high temperature.

Fig. 5 shows that  $D_g/D_0$  increases until a parabolic type peak appears and then decreases as  $a_w$  increases. This behavior can be explained by the combined mechanism of moisture sorption and water clustering. In the sorption region with low humidity, the moisture diffusion increases because the hydrogel becomes swollen with higher mobility of water molecules. The decrease in  $D_g/D_0$  at higher humidity is caused by the effect of cluster formation of water molecules, as mentioned above. Our framework developed in this study is practically useful to estimate the water diffusion in polymer hydrogel.

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