Temperature Effect on Drying and Swelling of Kappa Carrageenan Gels: A Steady State Fluorescence Study

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Summary: A novel technique based on in situ steady state fluorescence (SSF) measurements is introduced for studying drying and swelling of κ- carrageenan (kappa carrageenan) gels at various temperatures. κ- carrageenan gels were completely dried and then swelled in water vapor. Pyranine was embedded in κ- carrageenan and used as a fluorescence probe. Scattered light intensities, I_{sc} and fluorescence intensities, I were monitored during the drying and swelling of κ- carrageenan gels. It was observed that the fluorescence intensity decreased linearly as drying time was increased. A simple model consisting of Case II diffusion was used to quantify the drying processes of the κ- carrageenan gels. This moving boundary model provided packing constant, k_0. During swelling, fluorescence intensity increased exponentially as time is increased. The increase in I, was modeled using Li-Tanaka equation from which swelling time constants, τ_c and cooperative diffusion coefficients, D_c were determined. It was observed that swelling time constants, τ_c decreased and diffusion coefficients, D_c increased as the swelling temperature was increased. Activation energies for drying and swelling were also obtained and found to be 53.9 and 47.2 kJ mol^{-1}, respectively.

Keywords: cooperative diffusion coefficients; drying; fluorescence; κ- carrageenan; swelling

Introduction

Two network phases of different degree of swelling can exist and the transition from one state of network to the other is called volume phase transition.[1] Volume phase transitions in gels may occur from dry to swollen states, either continuously, or by sudden jumps between them.[2,3] The swelling, shrinking and drying kinetics of physical gels are important in many technological applications. Especially in pharmaceutical industries in designing controlled release of drugs and in using cosmetic ingredients, understanding the kinetics of gels is highly desirable. The knowledge of the gel kinetics is an important requirement for producing storable foods in agricultural industry and developing artificial organs in medical applications. In general the elastic and swelling properties or permanent networks can be understood by considering two opposing effects: osmotic pressure and restraining force.[4–6] Usually the total free energy of a chemically crosslinked network can be separated into two terms: bulk and shear energies. In a swollen network the characteristic quantity of the bulk free energy is the osmotic bulk modulus, K. The shear energy as the other important energy, keeps the gel in shape by minimizing the non-isotropic deformation. The characteristic coefficient of these forces is the shear modulus, G which can be most directly evaluated by stress–strain measurements.[7]

The theory of kinetics of swelling for a spherical chemical gel was first developed by Tanaka and Fillmore.[4] They assumed that the shear modulus G is negligible compared to the osmotic bulk modulus. However,

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several studies have shown that the shear modulus is the same order of magnitude as the osmotic bulk modulus.[8,9] Later, Peters and Candau have derived a model for the kinetics of swelling of spheres, cylinders and disks made of polymer gels by assuming non-negligible shear modulus.[10] Li and Tanaka have developed a model where the shear modulus plays an important role that keeps the gel in shape due to coupling of any change in different directions.[11] This model predicts that the geometry of the gel is an important factor, and swelling is not a pure diffusion process.

Several experimental techniques have been employed to study the kinetics of swelling, shrinking and drying of chemical and physical gels, e.g. neutron scattering[12], quasielastic light-scattering[10], macroscopic experiments[13] and in situ interferometric[14] measurements. Hawlader et al.[15] used a one-dimensional diffusion model to describe the heat and mass transfer in the wet and dry regions of materials undergoing shrinkage during drying. Coumans[16] has provided an excellent tutorial overview of the uses of the diffusion equation to analyze drying characteristic of slabs, including lumped diffusion models, retreating front models, and the characteristic drying curve model. The method given by Coumans relates to porous and nonporous materials. Some of these models also enable the evaluation of moisture dependent diffusivities from experimental drying curves of slabs. Steady state and time-resolved fluorescence techniques were applied to drying process of selected silane gels in oxygen free atmosphere. A kinetic model of drying was suggested and drying rate constants were determined.[17] The steady-state fluorescence technique was performed for studying drying and swelling kinetics in disc shape gels[18–21]. Recently, fast transient fluorescence (FTRF) technique was used in our laboratory to study gel swelling[22,23] and drying[24,25] processes.

In this work, we studied drying and swelling of κ- carrageenan gels at various temperatures by using steady-state fluorescence technique. κ- carrageenan gels doped with pyranine were completely dried and then swelled in water vapour. Drying of these gels were quantified by employing moving boundary model from which linear relaxation constants, k_0 were determined. Li-Tanaka equation was used to determine the swelling time constants, τ_c and cooperative diffusion coefficients, D_c for the swelling processes. It was observed that swelling time constant, τ_c decreased and cooperative diffusion coefficients, D_c increased as the swelling temperature increased.

Theoretical Considerations

Kinetics of Drying

The linear transport mechanism is characterized by the following steps. As the water molecules desorp from the gel, that is, as the gel starts drying, a moving boundary forms. This boundary proceeds with a constant velocity.

Now, consider a cross section of a gel with thickness d, under going Case II Diffusion[26] as in Figure 1, where L is the position of the advancing desorption front, C_0 is the initial molecule concentration and k_0 (mg/cm^{2}min) is defined as the packing constant. In fact, here k_0 represents the parameter for the packing of helices during drying of the gel. The kinetic expression for the desorption in the slab of an area A is given by

$$\frac{dM_t}{dt} = -k_0 A \tag{1}$$

where the amount of water molecules, M_t at time t is given by

$$Mt = -\int_0^t k_0 A dt + M_0 \tag{2}$$

here $M_0 = C_0 A d$ is the initial amount of water molecules trapped in the swollen gel at time zero. The amount of desorbed molecules at time t, can be written as

$$(M_0 - M_t) = k_0 A t \tag{3}$$

Since $M_t = C_0 A L$, then Equation (3) provides

$$C_0 A(d - L) = k_0 A t \tag{4}$$

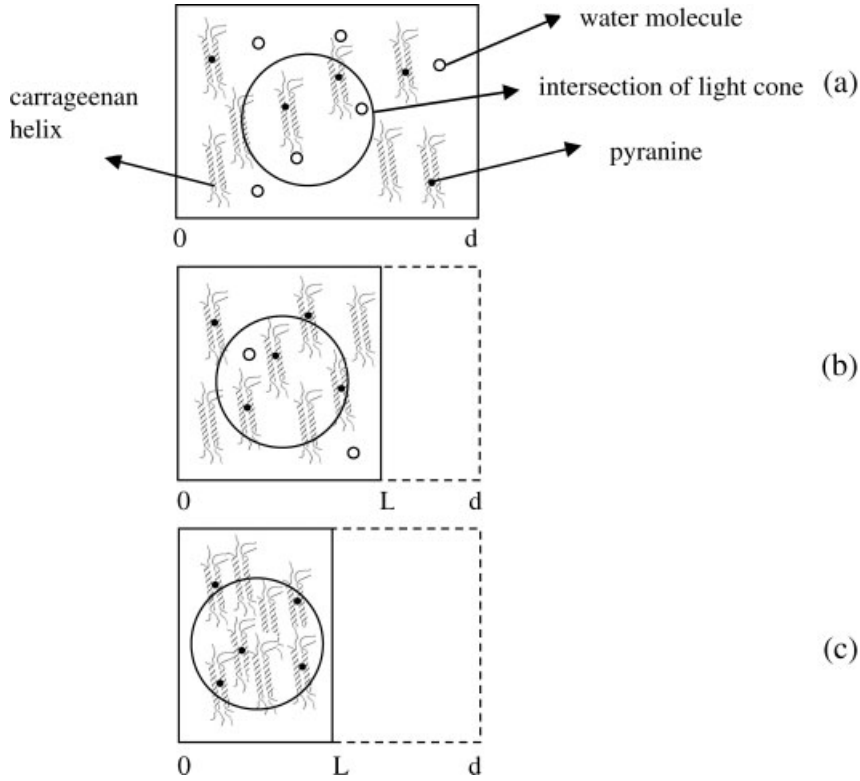

Figure 1.
A schematic representation of drying process (a) swollen gel, (b) drying gel and (c) dried gel.

The time derivative of Equation (4) produces the following relation

$$\frac{dL}{dt} = -\frac{k_0}{C_0} \tag{5}$$

Equation (5) can predict that the packing front, position at L, moves toward the origin with a constant velocity, k_0/C_0. The algebraic relation for L as a function of time, t is then described by Equation (6)

$$L = -\frac{k_0}{C_0}t + d \tag{6}$$

Kinetics of Swelling

Li and Tanaka[11] showed that the kinetics of swelling and shrinking of a polymer network or gel obey the following relation,

$$\frac{W(t)}{W_\infty} = 1 - \sum_{n=1}^{\infty} B_n e^{-t/\tau_n} \tag{7}$$

where W(t) and W_∞ are the degree of swelling or solvent uptake at time t and at infinite equilibrium, respectively. Here B_n represents a constant related to the ratio of the shear modulus, G and the longitudinal osmotic modulus, M is defined by the combination of shear and osmotic bulk modulus as $M = (K + 4G/3)$ and τ_n is the swelling rate constant. In the limit of large t or if τ_1 is much larger than the rest of τ_n, all higher terms ($n \geq 2$) in Equation (7) can be neglected, then Equation (7) becomes

$$\frac{W(t)}{W_\infty} = 1 - B_1 e^{-t/\tau_c} \tag{8}$$

Here B_1 is given by the following relation[11]:

$$B_1 = \frac{2(3-4R)}{\alpha_1^2 - (4R-1)(3-4R)} \tag{9}$$

where $R = G/M$ and α_1 is given as a function of R, i.e.

$$R = \frac{1}{4}\left[1 + \frac{\alpha_1 J_0(\alpha_1)}{J_1(\alpha_1)}\right] \quad (10)$$

where J_0 and J_1 present Bessel functions. In Equation (8), τ_c is related to the collective cooperative diffusion coefficient D_c of a gel disk at the surface and given by the relation

$$D_c = \frac{3a_\infty^2}{\tau_c \alpha_1^2} \quad (11)$$

Here, a_∞ is the half thickness of the gel in the final equilibrium state. Once the quantities τ_c and B_1 are obtained, R, α_1, and D_c can be calculated.

Experimental Part

Carrageenan (Sigma) at 3% (wt) concentration and pyranine were dissolved in distilled water (pH 6.5) by heating. The pyranine concentration were kept at 4×10^{-4} M, which is low enough to ensure that any excitation transfer effects are negligible. The heated carrageenan solution was held at 80 °C and was continuously stirred by a magnetic stirrer. Then this solution was cooled down to room temperature. After the gels were formed, we cut the gel samples into disc shape gels to use in drying. Disc-shaped gel samples were placed on the wall of 1×1 quartz cell for the drying and swelling experiments. In fluorescence spectrometer the position of the gel and the incident light beam, I_o for the fluorescence measurements are shown in Figure 2a during drying in air. In Figure 2b the position of the gel during swelling in water vapor is presented. These gels were first dried at 30, 40, 50 and 60 °C respectively before the swelling measurements started. The drying and swelling experiments of κ- carrageenan gels were performed at temperatures of 30, 40, 50 and 60 °C respectively. The fluorescence intensity measurements were carried out using the Model LS-50 spectrometer of Perkin-Elmer, equipped with temperature controller.

All measurements were made at 90° position and slit widths were kept at 5 nm. Pyranine was excited at 460 nm during *in situ* experiments and emission intensities of the pyranine were monitored at 515 nm as a function of drying and swelling time. Typical spectra of pyranine at various drying and swelling times are presented in Figure 3a and Figure 3b, respectively.

Results and Discussion

Drying

Scattered light, I_{sc} and fluorescence intensities, I during drying of κ- carrageenan gels for the various temperatures are presented in Figure 4 and Figure 5 respectively.

It is seen in Figure 4 and Figure 5 that the fluorescence intensities decreased as the scattered light intensity increased, predicted that gel becomes turbid during drying. Figure 1 shows that as water molecules

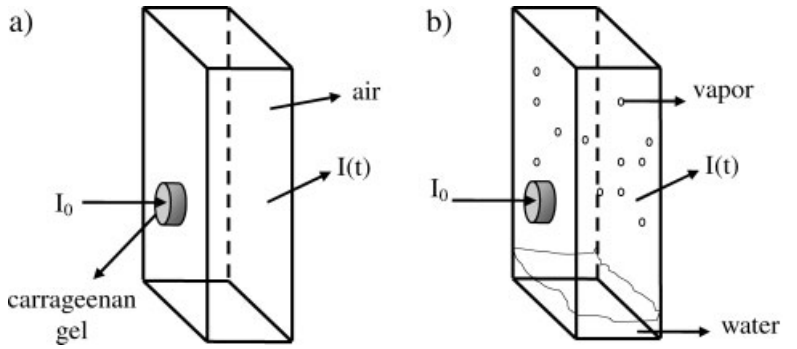

Figure 2.
The position of κ- carrageenan gel in the fluorescence cell (a) during drying, (b)during swelling in water vapour. I_o is the excitation and $I(t)$ is the emission intensities at 460 nm and 515 nm, respectively.

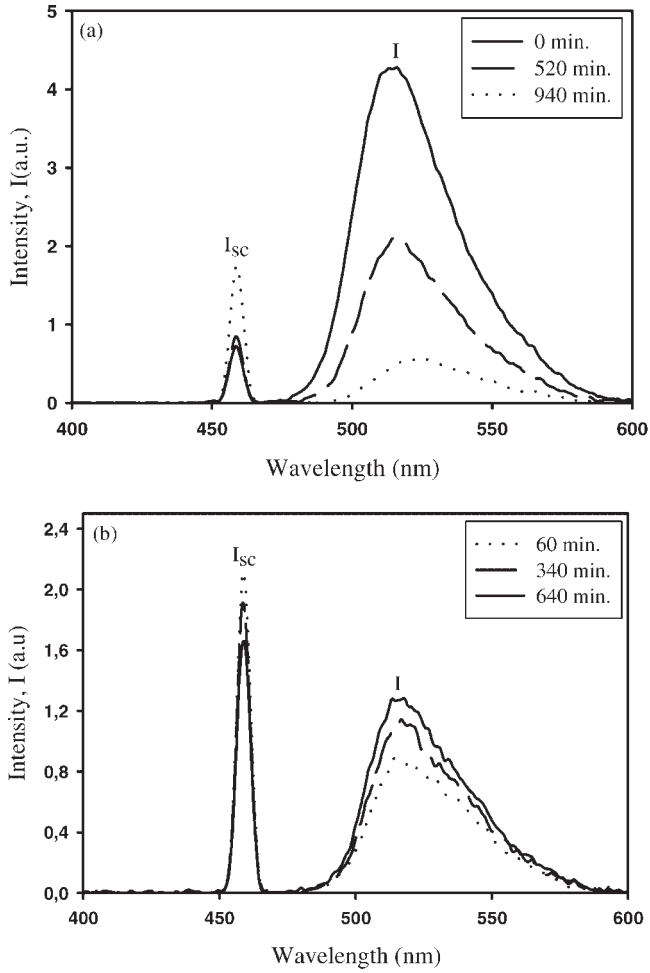

Figure 3.
Fluorescence spectra of pyranine during (a) drying, (b) swelling.

desorp from the drying gel double helices pack and crowd into the light cone (incident light I_0) intersection. Crowding helices prevent the incident light beam to penetrate into the gel sample. As a result less pyranine molecules can be excited, which cause a decrease in the fluorescence light intensity. Since drying occurs in the gel state of κ- carrageenan, no quenching of pyranine molecules are expected. In other words pyranine molecules are assumed to be buried in the double helices.

This behavior of fluorescence intensity, I during drying can be modeled by using Equation (3), where M_0 and M values are assumed to be proportional to I_0 and I values at time zero and at time t. Then, Equation (3) becomes

$$\frac{I_0 - I}{I_0} = \frac{k_0}{C_0 d} t \tag{12}$$

Organizing Equation (12) provides us with a very useful relation

$$\frac{I}{I_0} = 1 - \frac{k_0}{C_0 d} t \tag{13}$$

Equation (13) predict that fluorescence intensity decreases linearly as the drying time is increased, due to packing of double helices i.e. due to increasing turbidity of carrageenan gel which scatters the incident light. Fitting Equation (13) to the data in

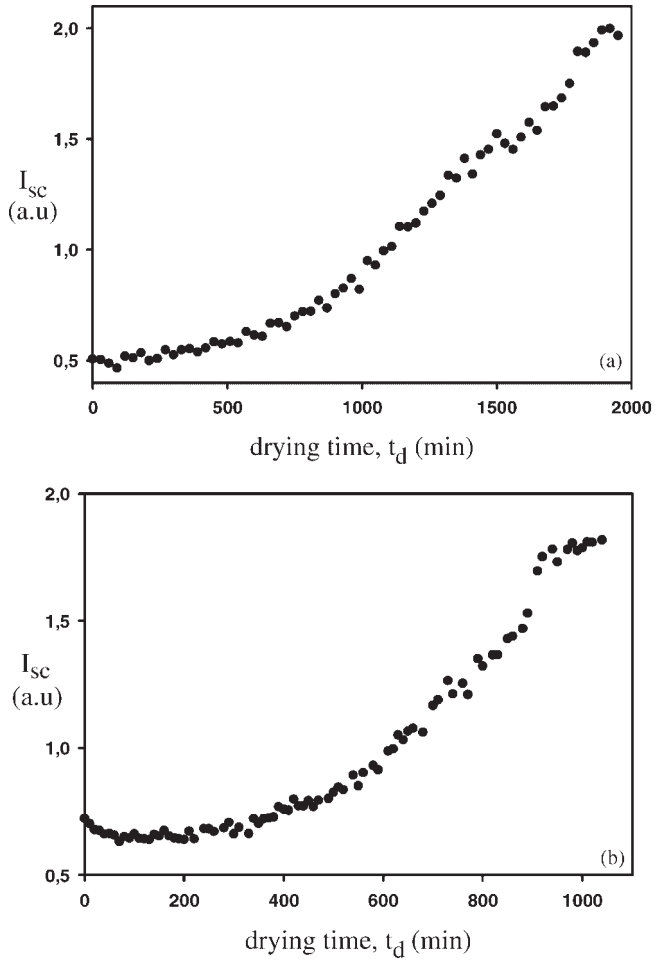

Figure 4.
Scattered light intensities of pyranine at (a) 30 and (b) 40 °C during drying time

Figure 5 produces k_0 values which are listed in Table 1 together with the other measured parameters of the gel samples where d is the diameter, a_i and a_∞ are the thickness, m_i and m_∞ are the weights of the gel before and after the drying process. It is seen that k_0 value increases as the temperature is increased, as expected, helices can be packed faster at higher temperatures.

The temperature-dependence of the packing constant, k_0, for the helices can be treated by the well-known Arrhenius relation given below

$$k_0 = k_{00}e^{-\Delta E/kT} \quad (14)$$

where ΔE is the energy for packing process of carrageenan gel, k is the Boltzmann constant, T is the temperature and k_{00} is the pre exponential factor. Figure 6 present the fitting of Equation (14) to the k_0 data in Table 1. The activation energy, ΔE measured from the fluorescence intensity is found to be 53.9 kJ mol^{-1}.

Swelling

The plots of fluorescence, I and scattered light intensities versus time during swelling of κ- carrageenan gels at various temperatures are presented in Figure 7 and Figure 8, respectively. It is seen that fluorescence intensity increased, however, scattered light

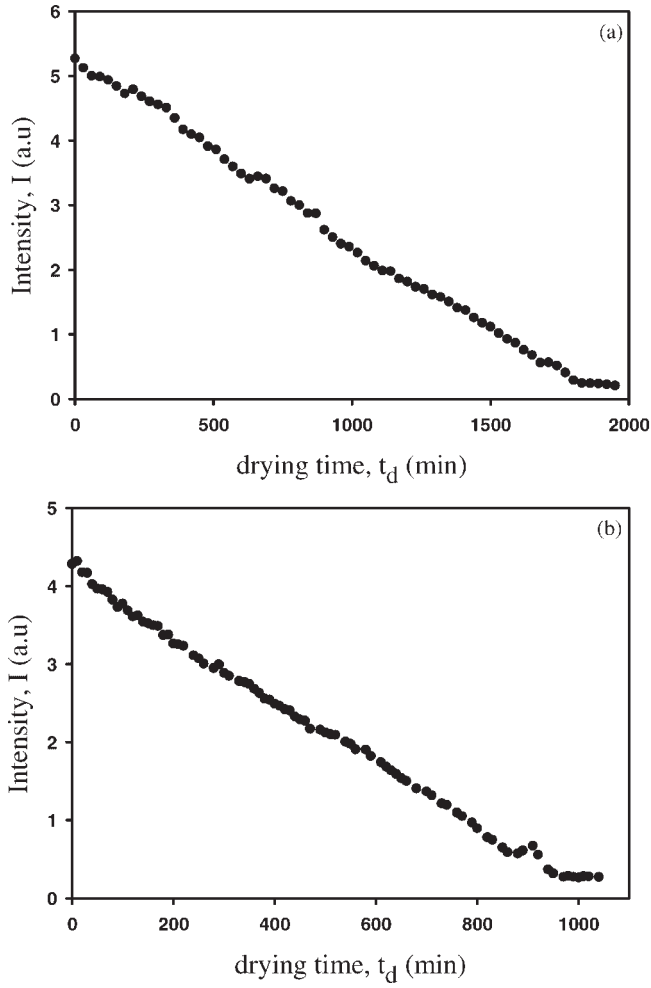

Figure 5.
Fluorescence intensities of pyranine at (a) 30 and (b) 40 °C during drying time.

intensity decreased during swelling. Since the transmitted light intensity, $I_{tr} = 1 - I_{sc}$ increases, the gel became transparent, as a result I increases.

Here since swelling occurs in gel state of carrageenan then one has to assume that pyranine molecules are embedded in the helices, so that no quenching can take place.

Table 1.
Experimentally obtained drying parameters.

Gel properties	Temperature			
	30 °C	40 °C	50 °C	60 °C
a_i (mm)	3.3	3.2	3.35	3.2
a_∞ (mm)	0.45	0.7	0.8	0.90
m_i (g)	0.201	0.208	0.2055	0.1825
m_∞ (g)	0.0108	0.0104	0.0102	0.0085
d(mm)	8.85	8.7	8.8	8.8
$k_o \times 10^{-8}$ ($mm^2g^{-1}s^{-1}$)	3.37	5.29	14.3	20.6

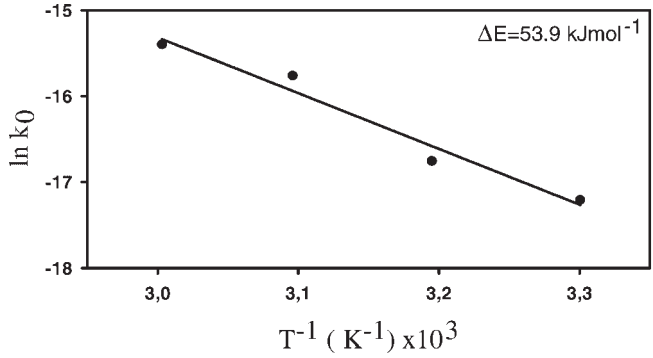

Figure 6.
The logarithmic plot of k_o values versus temperature T^{-1} according to Equation. (14). The slope of the linear relation produces the activation energy, ΔE for drying process.

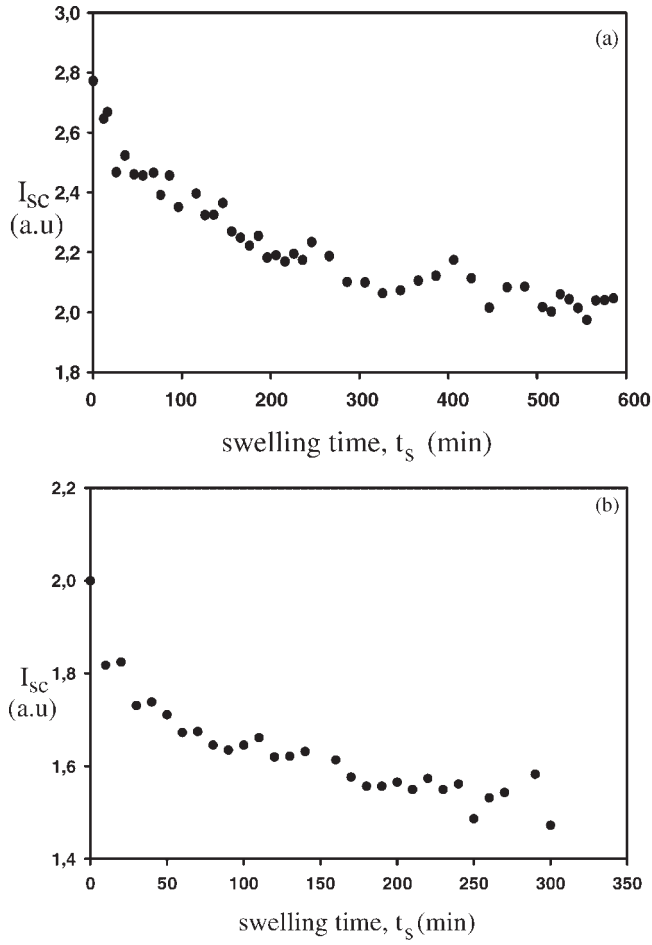

Figure 7.
Scattered light intensities of pyranine at (a) 30 and (b) 50 °C during swelling time

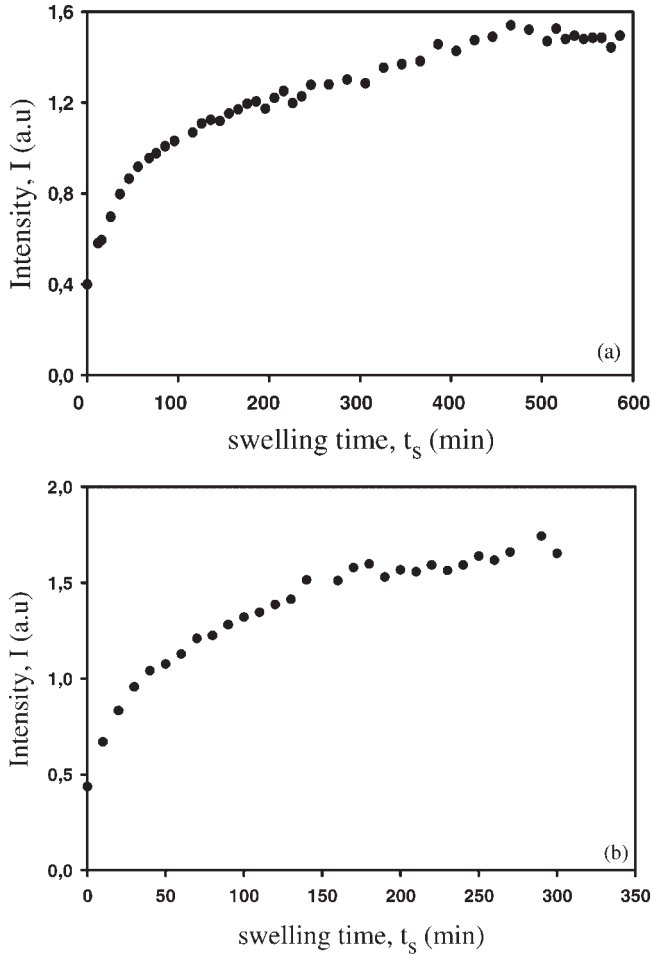

Figure 8.
Fluorescence intensities of pyranine at (a) 30 and (b) 50 °C during swelling time.

At the equilibrium state of swelling, the fluorescence intensity reaches I_∞, where the vapor uptake is W_∞. The relation between the vapor uptake W and the fluorescence intensity, I is then given by

$$\frac{W}{W_\infty} = \frac{I}{I_\infty} \tag{15}$$

This relation predicts that as W increases, I increases. Combining Equation (15) with Equation (8) and calculating the logarithm of them, the following relation can be obtained

$$\ln\left(1 - \frac{I}{I_\infty}\right) = \ln B_1 - \frac{t_s}{\tau_c} \tag{16}$$

where $t = t_s$ is taken in Equation (8) to present the swelling time in Equation (16). Logarithmic plots of $(1 - \frac{I}{I_\infty})$ are presented in Figure 9. Linear regression of curves in Figure 8 provides us with the B_1 and τ_c values from Equation (16).

Taking into account the dependence of B_1 on R, one obtains R values and from α_1-R dependence, α_1 values were produced. Then using Equation (11) cooperative diffusion coefficients D_c were determined for these disc-shaped carrageenan gels. Experimentally obtained τ_c and D_c values for kappa carrageenan gels at various temperatures are presented in Table 2. It is seen in Table 2 that as temperature is increased, time constant, τ_c presented a

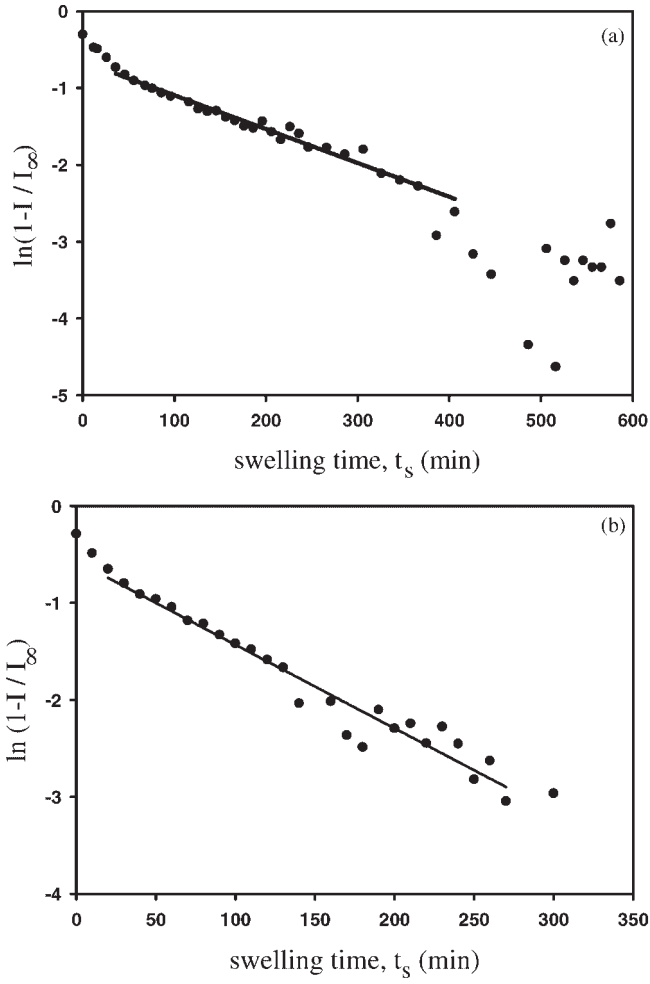

Figure 9.
Logaritmic plots of *I*, according to Equation (16) for κ- carrageenan gels in water vapour at (a) 30 and (b) 50 °C during swelling time.

decrease as expected, i.e. the time for the network homogenization decreased as the temperature is increased. Here we note that decrease in I_{sc} (increase in I_{tr}) may correspond to homogenization of the gel network, which produce high transparency.

The behavior of D_c versus temperature predicts that gel segments (helices) move

Table 2.
Experimentally obtained swelling parameters.

Gel properties	Temperature			
	30 °C	40 °C	50 °C	60 °C
a_i (mm)	0.45	0.7	0.8	0.90
a_∞ (mm)	1.6	1.6	1.7	1.9
m_i (g)	0.0108	0.0104	0.0102	0.0085
m_∞ (g)	0.03	0.0327	0.0332	0.0056
τ_c (min)	298	196	109	87
$D_c \times 10^{-7}$ ($cm^2 s^{-1}$)	2.24	3.43	7.22	11.4

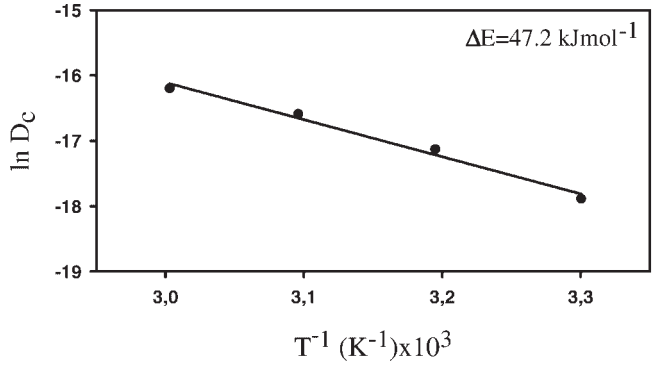

Figure 10.
The logarithmic plot of D_c values versus temperature T^{-1} according to Eq. (17). The slope of the linear relation produces the activation energy, ΔE for swelling process.

much faster at higher temperatures during vapor penetration. As seen in Table 2, D_c values increased as the temperature is increased, predicts that the D_c-T relation may obey the following Arrhenius law.

$$D_c = D_{c0} \exp(-\Delta E/kT) \qquad (17)$$

where the ΔE is named as the activation energy for swelling, k is the Boltzmann's constant and D_{co} is the cooperative diffusion coefficient at $T = \infty$. The logarithmic form of the D_c is plotted versus T^{-1} in Figure 10, where the slope of the linear relation produces the activation energy, ΔE for the swelling gel as 47.2 kJ mol^{-1}.

Conclusion

In summary, this paper presents a novel method for studying drying and swelling kinetics of κ- carrageenan gels at various temperatures. Case II diffusion model was used to measure the packing constants, k_0 during drying and the activation energy, ΔE for drying process. Also the swelling time constants, τ_c and the cooperative diffusion coefficients, D_c were measured during the swelling of κ- carrageenan gels by using Li-Tanaka model. It was observed that swelling time constant, τ_c decreased and cooperative diffusion coefficients, D_c increased as the swelling temperature increased. D_c values were used to obtain the swelling activation energy. It is interesting to note that the swelling activation energy was found to be smaller than the drying activation energy, indicating that the energy need for packing of helices is higher than unpacking of them. In other words contribution of hydrogen bonding to the swelling process was found to be much less than during drying process.

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