Polym. Bull. (2011) 66:529–539
DOI 10.1007/s00289-010-0362-2

ORIGINAL PAPER

Fluorescence study on drying of ι-carrageenan gels at different temperatures prepared with various $CaCl_2$ content

Ozlem Tari · Onder Pekcan

Received: 17 October 2008 / Revised: 29 July 2010 / Accepted: 31 July 2010 /
Published online: 7 August 2010

Abstract The influence of temperature and salt content on drying was investigated by using steady-state fluorescence (SSF) technique. Supporting gravimetric and volumetric measurements were also carried out during drying of gels at various temperatures. ι-Carrageenan gels were prepared with various $CaCl_2$ content. Pyranine was introduced as a fluorescence probe during gel preparation. Apparent fluorescence intensity, I, was measured during in situ drying process at each temperature and it was observed that fluorescence intensity values decreased for all gel samples. A simple model consisting of Case II diffusion was used to produce the packing constants, k_0, for helixes. It was observed that k_0 increased as the drying temperature was increased. On the other hand at each temperature, it was seen that k_0 decreased as $CaCl_2$ content was increased. Packing energies for drying processes were obtained from fluorescence, volumetric, and gravimetric measurements separately.

Keywords Fluorescence · Drying · Carrageenan · Diffusion · Packing

Introduction

Carrageenans are linear heteropolysaccharides made up of repeating galactose units and 3,6-anhydro-D-galactose (3,6-AG). They are differentiated by the number and the position of ester sulfate groups and the amount of 3,6-anhydro-D-galactose which they contain [1]. They come in three major types designated by means of Greek letters as κ, ι, and λ. They are well known for their gel forming properties and

O. Tari
Department of Physics, Istanbul Technical University, Maslak 34469, Istanbul, Turkey

O. Pekcan (✉)
Kadir Has University, Cibali 34980, Istanbul, Turkey
e-mail: pekcan@khas.edu.tr

are used extensively in food and pharmaceutical industry as gelling or thickening agents [2]. κ-Carrageenan and ι-carrageenan undergo a temperature dependent coil (disordered state) to helix (ordered state) transition in aqueous solution. κ-Carrageenan usually forms firm, brittle gels and it is sensitive to potassium ions. ι-Carrageenan usually generates soft, elastic gels and it is sensitive to calcium ions.

Several studies have dealt with the swelling, shrinking, and drying kinetics [3–5]. In fact, the swelling, shrinking, and drying kinetics of chemical and physical gels are very important in many applications, such as in designing controlled release devices for oral drugs, cosmetic ingredients, in producing storable foods and in developing artificial organs. Electrochemical and gravimetric methods have already been used in studies of ions release from ι-carrageenan gels or tablets [6, 7]. NMR spectroscopy is used to investigate the diffusion phenomenon of an aroma molecule in ι-carrageenan gels by Rondeau-Mouro et al. [8].

Diffusion in polymer systems is a complicated process. It depends on the properties of diffusants, the polymer network, and the solvents. Various models and theories are proposed [9]. One-dimensional diffusion model was used to describe heat and mass transfer within materials undergoing shrinkage during drying [10]. Miller used fluorescence techniques to study drying process of selected silane gels in oxygen free atmosphere. A kinetic model of drying was suggested and drying rate constants were determined [11]. Coumans [12] 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. The steady-state fluorescence technique was performed for studying drying and swelling kinetics in disk-shaped gels [13–16]. Recently, fast transient fluorescence (FTRF) technique was used in our laboratory to study gel swelling [17, 18] and drying [19] processes.

In this paper, we will present the results of fluorescence measurements of the drying of ι-carrageenan gels prepared in varies concentrations of $CaCl_2$. Drying of these gels at different temperatures was quantified by employing moving boundary model from which linear packing constants, k_0, were determined. Gravimetric and volumetric measurements were performed for all gel samples in the same conditions. The packing energies, ΔE, of drying were obtained separately from fluorescence, volumetric, and gravimetric measurements.

Theoretical considerations

In this study, we employed a simple model based on Case II diffusion, developed by Enscore et al. [20], to interpret the drying experiments of ι-carrageenan gels performed at various temperatures where 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.

Consider a cross section of a gel with thickness d, under going Case II diffusion as in Fig. 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 from 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 the following relation:

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

here $M_0 = C_0 Ad$ 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

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

Since $M_t = C_0 AL$, then Eq. 3 provides

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

The time derivative of Eq. 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 Eq. 6

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

Experimental

ι-Carrageenan (Sigma) at 2% (wt) concentration and pyranine were dissolved in various $CaCl_2$ solutions by heating. Pyranine concentration was taken as 4×10^{-4}M for all samples. The heated carrageenan solution was held at 80 °C and was continuously stirred by a magnetic stirrer and then transferred into syringe and cooled down to room temperature. Four different gels were prepared with various $CaCl_2$ contents ranging from 0.6, 0.8, 1.0, and 1.2% (wt). These samples are named as 2I06Ca, 2I08Ca, 2I1Ca, and 2I12Ca, respectively. Disk-shaped gels were obtained by cutting the cylindrical gel. Gels in various $CaCl_2$ contents were placed on the wall of 1 × 1 quartz cell for the fluorescence experiments as shown in Fig. 2.

The fluorescence intensity measurements were carried out using the Model LS-50 spectrometer of Perkin-Elmer, equipped with temperature controller. This cell was placed in the spectrometer and fluorescence emission was monitored at 90° angle.

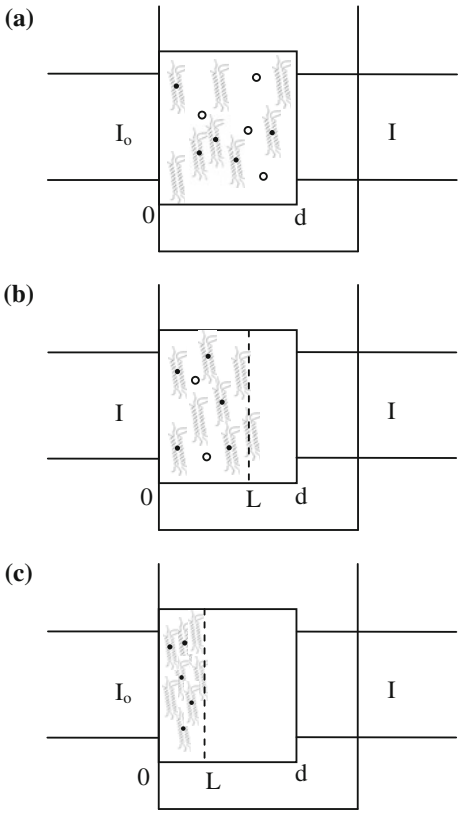

Fig. 1 A schematic representation of drying process. **a** Swollen gel, **b** drying gel, and **c** dried gel. I_o and I represent the excitation and emission intensities

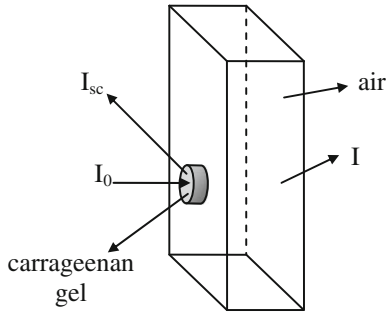

Fig. 2 The position of *ι*-carrageenan gel in the fluorescence cell during drying, I_o is the excitation and I is the emission intensities

The position of the gel and the scattered, I_{sc}, incident, I_o, and emission, I, light beams for the fluorescence measurements are shown in Fig. 2, during drying in air. Drying experiments were carried out separately at temperatures 30, 40, 50, and 60 °C, respectively. Emission intensities, I, of the pyranine were monitored as a function of drying time, t_d, at various temperatures. Typical spectra of pyranine at various drying times are presented in Fig. 3.

As control experiments, gravimetric and volumetric measurements were performed at the same condition as fluorescence measurements were done. Weights,

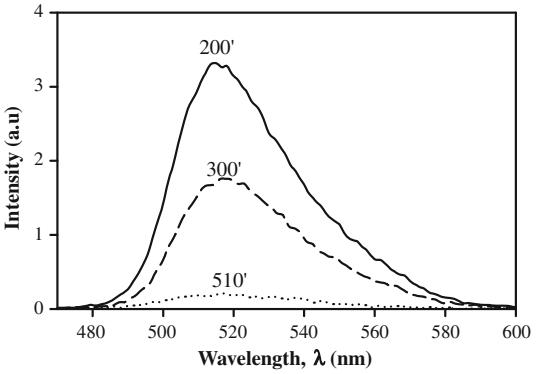

Fig. 3 Fluorescence spectra of pyranine during drying. *Numbers* on each curve indicate the drying time in min

thicknesses, and radii of the gel samples were monitored by using microbalance and calipers. In this work, we used two identical disk-shaped gels. One of them was placed in the cell of the spectrometer for the fluorescence measurements and in the mean time, the other one was used for the gravimetric and volumetric measurements.

Results and discussion

Fluorescence, I, and scattered light, I_{sc}, intensities against drying time, t_d, are presented in Figs. 4 and 5a for the 2I1Ca gel dried at various temperatures, respectively.

It is seen in Figs. 4 and 5a that the fluorescence intensity decreased as the scattered light intensity increased during drying. On the other hand, Fig. 1 shows that as water molecules desorp from the drying gel double helices pack and crowd into the incident light beam, I_0, by creating stiffer environment. The gel thickness in the direction of incident light decreases more than the gel radius which keeps the number of pyranines constant in the incident beam. These crowding helices increase the turbidity of the gel and prevent the incident light beam to penetrate into the gel sample by increasing the scattered light intensity. As a result, less pyranine

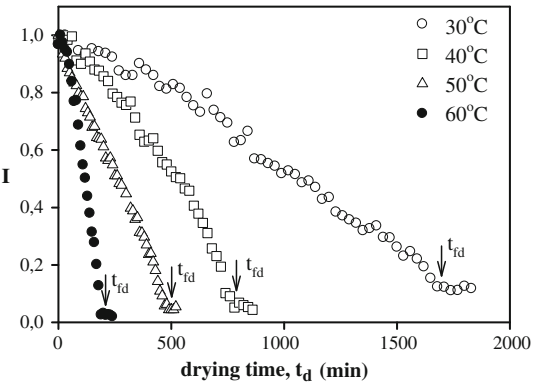

Fig. 4 Fluorescence intensities, I, of pyranine versus drying time, t_d, at various temperatures

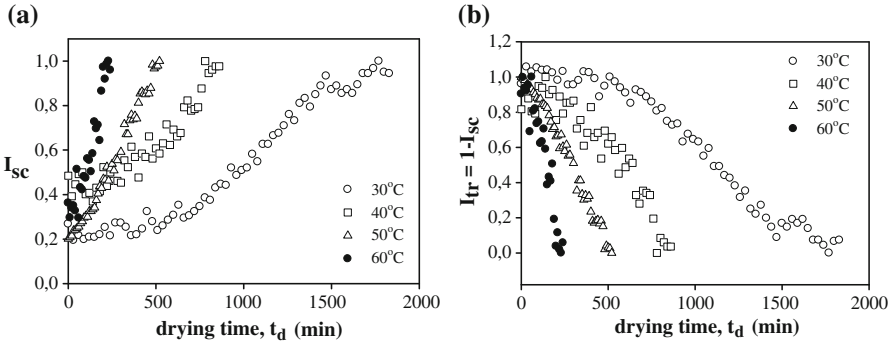

Fig. 5 **a** Scattered, I_{sc}, **b** transmitted, I_{tr}, light intensities of pyranine versus drying time, t_d, at various temperatures

molecules can be excited, which cause a decrease in the fluorescence light intensity. In other words, pyranine molecules embedded in the double helices cannot be excited due to increase in light scattering.

This behavior of fluorescence intensity, I, during drying can be modeled by using Eq. 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_d. Then, Eq. 3 becomes

$$\frac{I_0 - I}{I_0} = \frac{k_0}{C_0 d} t_d \tag{7}$$

Organizing Eq. 7 provides us with a very useful relation

$$\frac{I}{I_0} = 1 - \frac{k_0}{C_0 d} t_d \tag{8}$$

This relation predicts that fluorescence intensity decreases linearly as the drying time increases due to packing of double helices, i.e., due to increasing turbidity of carrageenan gel, which scatters the incident light. Linear least square fitting procedure was applied to the data in Fig. 4 with the correlation coefficient around 0.98. Fitting of Eq. 8 to the data in Fig. 4 produces k_0 values which are listed in Table 1 together with the other measured parameters of the gel samples where a is

Table 1 Experimentally determined drying parameters of 2I1Ca gel at various temperatures

Gel properties	Temperature (°C)			
	30	40	50	60
d_i (mm)	2.4	2.35	2.4	2.4
d_∞ (mm)	0.35	0.45	0.45	0.35
m_i (g) $\times 10^{-2}$	13.63	12.44	12.06	11.28
m_∞ (g) $\times 10^{-2}$	0.48	0.57	0.42	0.23
a (mm)	9	8.65	8.9	8.9
$k_0 \times 10^{-8}$ (mm^2 g^{-1} s^{-1})	2.12	3.97	9.15	17.2
$k_{0m} \times 10^{-8}$ (mm^2 g^{-1} s^{-1})	2.94	6.85	13.2	23.9
$k_{0v} \times 10^{-8}$ (mm^2 g^{-1} s^{-1})	2.58	6.85	14.0	25.2

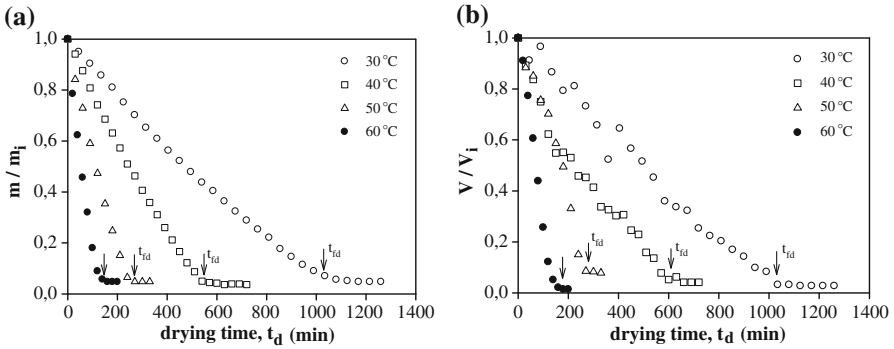

Fig. 6 Plots of **a** weights, m, and **b** volumes, V, of the ι-carrageenan gels versus drying time, t_d

the diameter, d_i and d_∞ are the initial and final thickness, m_i and m_∞ are the initial and final weights of the gel before and after the drying process is ended. It is seen that k_0 value increases as the temperature is increased, as expected, i.e., helices can be packed faster at higher temperatures. Here we have to also note that the time variation of the transmitted light intensity $I_{tr} = 1 - I_{sc}$ (Fig. 5b) is almost one to one corresponds to the time variation of fluorescence intensity as shown in Fig. 4. These behaviors confirm our prediction about the evolution of turbidity due to helix packing, which results in the decrease in transmitted light intensity, I_{tr}, during drying.

The time behavior of the weights, m, and volumes, V, of the ι-carrageenan gels during drying are presented in Fig. 6a, b, respectively. The volumetric measurements were performed by measuring the radii and the thicknesses (d_i, d_∞) of the gels separately. It is seen that both weights and volumes of the gel decrease linearly by obeying the following relations predicted with Eq. 8.

$$\frac{m}{m_i} = 1 - \frac{k_{0m}}{C_0 \mathrm{d}}\, t_\mathrm{d} \tag{9}$$

$$\frac{V}{V_i} = 1 - \frac{k_{0V}}{C_0 \mathrm{d}}\, t_\mathrm{d} \tag{10}$$

Here k_{0m} and k_{0V} are the weight and volume packing constants, m_i and V_i are the initial values of weight and volume, t_d represents the drying time. Linear least square fitting of Eqs. 9 and 10 to the data in Fig. 6a, b produces k_{0m} and k_{0V} values, which are listed in Table 1. It is seen that k_{0m} and k_{0V} values also increase as the temperature is increased.

Careful examination of Figs. 4 and 6 shows that at low temperature (30 and 40 °C) drying curves deviate from linearity by presenting two distinct regions, which can be explained with the surface drying at early times, followed by the bulk drying at longer times, respectively. However at high temperatures (50 and 60 °C) bulk drying takes place immediately by showing single linear drying curves. In this work, only the long time regions were considered at low temperature drying for the fitting procedure, short time behaviors are omitted. The surface drying can be described as the slow organization of the surface helices due to water evaporation at

early times. On the other hand, bulk drying is simply the packing of helices by obeying the theoretical model given above.

Here one has to argue about the differences between k_0 and, k_{0m} and k_{0V} values, even though all are called as packing constants. It can be seen from Figs. 4 and 6 that macroscopic (bulk packing) drying of gels completed much earlier than that of microscopic (helix packing) drying at different temperatures. The fluorescence technique measures the behavior of the microstructural dynamic of the gel. In other words, fluorescence probes monitor the helical packing during gel drying. However, gravimetric and volumetric measurements can provide us with the information of macroscopic behavior (bulk dynamic) of the gel. Figure 7a–c compares the final drying times t_{fd} for microscopic (helix) and macroscopic (bulk) packing of drying in ι-carrageenan gels, respectively. It is seen that macroscopic drying is much faster than microscopic drying. It is understood that helix packing takes longer time than that of bulk packing, i.e., even though the gel is dried in bulk, it still needs longer time to organize its helices to be packed.

The plots of fluorescence intensity, I, versus time, during drying of 2I06Ca and 2I08Ca, are presented in Fig. 8a, b at 40 °C, respectively. Fittings of Eq. 8 to the data in Fig. 7 produced k_0 values. Experimentally produced k_0 values for the gels prepared at various $CaCl_2$ contents are presented in Table 2, where k_0 values for the low $CaCl_2$ content (loosely formed) gels are found to be larger than the high $CaCl_2$ content (densely formed) gels. Since densely formed gels possess more double helices, which then packed slower than loosely formed gels during drying. Final drying time, t_{fd}, for the loosely formed gel is also much shorter than densely formed gel as expected.

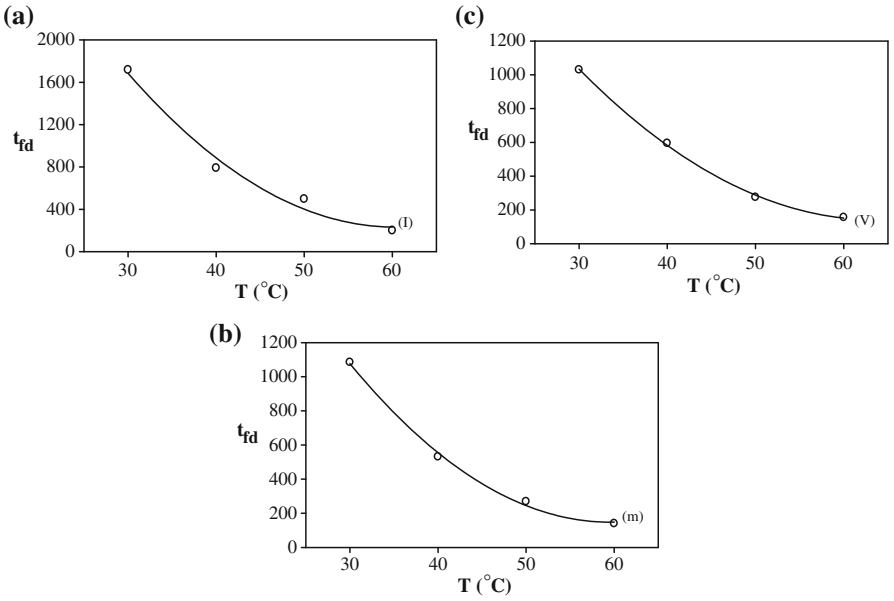

Fig. 7 Plot of final drying time t_{fd} versus temperature, T, for **a** fluorescence, I, **b** gravimetric, m, and **c** volumetric, V, measurements

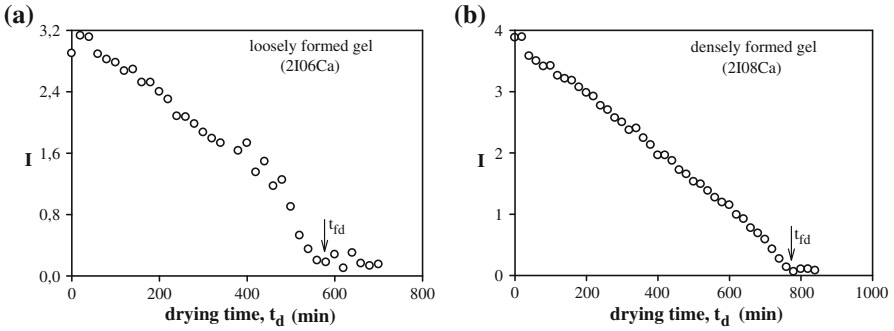

Fig. 8 Fluorescence intensities of pyranine versus drying time, t_d, at 40 °C for **a** 2I06Ca and **b** 2I08Ca gels

Table 2 Experimentally determined drying parameters of the gels prepared with various $CaCl_2$ content at 40 °C

Gel properties	$CaCl_2$ content (wt%)			
	0.6 (2I06Ca)	0.8 (2I08Ca)	1.0 (2I1Ca)	1.2 (2I12Ca)
d_i (mm)	2.35	2.45	2.35	2.45
d_∞ (mm)	0.4	0.35	0.45	0.35
m_i (g) $\times 10^{-2}$	12.05	13.38	12.44	12.07
m_∞ (g) $\times 10^{-2}$	0.52	0.34	0.57	0.50
a (mm)	8.95	9.25	8.65	8.95
$k_0 \times 10^{-8}$ (mm^2 g^{-1} s^{-1})	4.73	3.93	3.97	3.12
$k_{0m} \times 10^{-8}$ (mm^2 g^{-1} s^{-1})	7.72	7.42	6.85	4.93
$k_{0V} \times 10^{-8}$ (mm^2 g^{-1} s^{-1})	6.50	6.83	6.85	4.71

The whole picture for t_{fd} at different temperatures is summarized in Fig. 9. In general, we have observed that the packing rate increases with increasing temperature and decreases with increasing $CaCl_2$ concentration.

The packing energy of the drying process can be determined by fitting the experimental data to the Arrhenius equation given below

$$k_0 = k_{00} e^{-\Delta E/kT} \tag{11}$$

where ΔE is the energy for packing process of ι-carrageenan gel, k is the Boltzmann constant, T is the temperature, and k_{00} is the pre-exponential factor. The packing energies for the samples 2I06Ca, 2I08Ca, 2I1Ca, and 2I12Ca were determined from the slope of the linear plots in Fig. 10 and were found to be as 53.2, 57.0, 61.9, and 61.4 kJ mol^{-1}, respectively. Here it is seen that loosely packed gels need less energy than densely packed gels for the drying process. The activation energies were also calculated for gravimetric and volumetric measurements and found to be in between 48.0 and 60.9 kJ mol^{-1} indicating that energy needed for microscopic

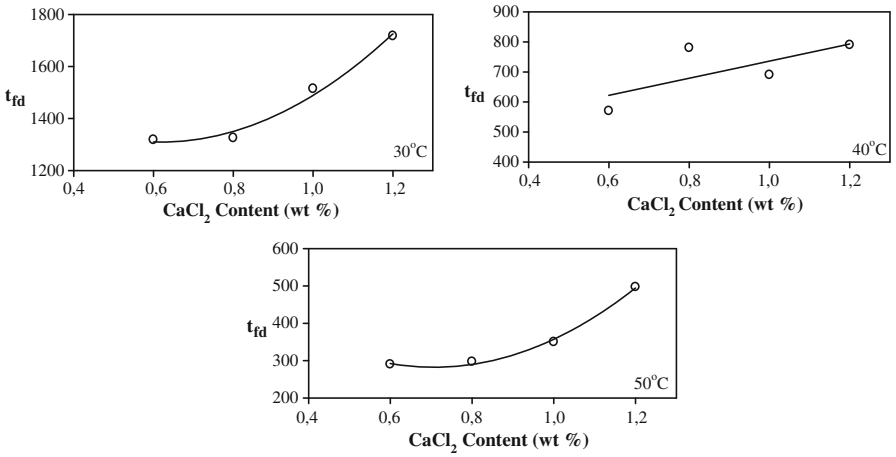

Fig. 9 Plot of final drying times t_{fd} versus $CaCl_2$ content at various temperatures

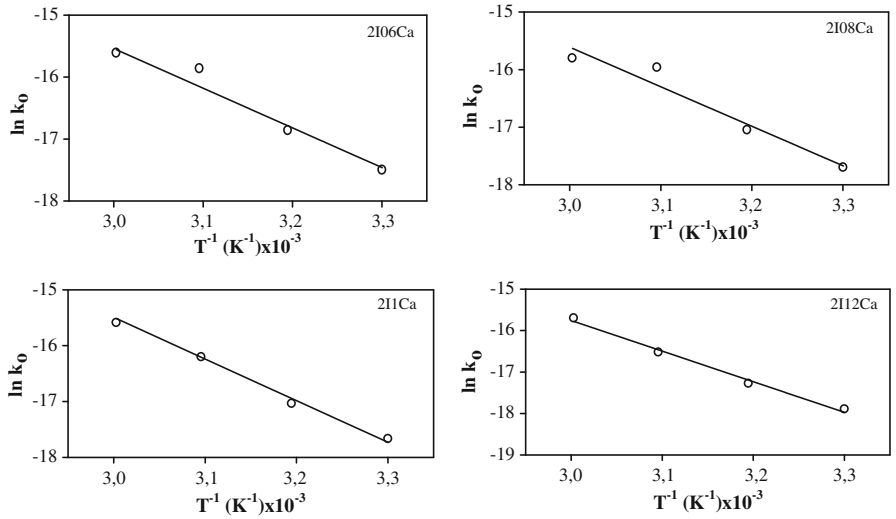

Fig. 10 The logarithmic plot of k_0 values versus temperature T^{-1} according to Eq. 14. The slope of the linear relation produces the activation energy, ΔE, for drying process

and macroscopic drying do not differ much. In other words, energy for helical and bulk packing is almost same even though their packing rates are different.

Conclusion

The results in this work have shown that the fluorescence method can be used to monitor drying process of ι-carrageenan gels. Linear time dependence of the

fluorescence intensity curves forced us to introduce the Case II diffusion model, which has produced nice fitting to our experimental result. It has been understood that both temperature and concentration affect the drying processes. The packing constants, k_0, k_{0m}, and k_{0V} were measured and found to obey the Arrhenius relation from which the activation energies were produced and found to be depending on $CaCl_2$ content, i.e., larger activation energies were found for higher $CaCl_2$ content gel samples.

References

1. Thomas WR (1999) Carrageenan. In: Imeson A (ed) Thickening and gelling agents for food. Aspen Publication, Gaithersburg, MA, pp 45–59
2. Piculell L (1995) Gelling carrageenans. In: Stephen AM (ed) Food polysaccharides and their applications. Marcel Dekker, New York, pp 205–244
3. Peters A, Candau SJ (1988) Kinetics of swelling of spherical and cylindrical gels. Macromolecules 21:2278–2282
4. Zrinyi M, Rosta J, Horkay F (1993) Studies on the swelling and shrinking kinetics of chemically crosslinked disk-shaped poly(vinyl acetate) gels. Macromolecules 26:3097–3102
5. Pekcan O, Kara S (2000) Lattice heterogeneities at various crosslinker contents—a gel swelling study. Polymer 41:8735–8739
6. Picker KM (1999) Matrix tablets of carrageenans. II. Release behavior and effect of added cations. Drug Dev Ind Pharm 25:339–346
7. Ciszkowska M, Guillaume MD (1999) Transport of ions and molecules in biopolymeric gels: electroanalytical studies. J Phys Chem A 103:607–613
8. Rondeau-Mouro C, Zykwinska A, Durand S, Doublier J-L, Buleon A (2004) NMR investigations of the 4-ethyl guaicol self-diffusion in iota (iota)-carrageenan gels. Carbohydr Polym 57:459–468
9. Masaro L, Zhu XX (1999) Physical models of diffusion for polymer solutions, gels and solids. Prog Polym Sci 24:731–775
10. Hawlader MNA, Ho JC, Qing Z (1999) A mathematical model for drying of shrinking materials. Temperature and moisture distribution within materials undergoing shrinkage during drying. Dry Technol 17:27–47
11. Miller E (2002) Investigation of drying silica gel by fluorescence methods. J Photochem Photobiol A 152:249–257
12. Coumans WJ (2000) Models for drying kinetics based on drying curves of slabs. Chem Eng Process 39:53–68
13. Pekcan O, Yilmaz Y (1996) Fluorescence method to study gelation swelling and drying processes in gels formed by solution free radical copolymerization. Prog Colloid Polym Sci 102:89–97
14. Yilmaz Y, Pekcan O (1998) In situ fluorescence experiments to study swelling and slow release kinetics of disc-shaped poly(methyl methacrylate) gels made at various crosslinker densities. Polymer 39:5351–5357
15. Erdogan M, Pekcan O (2000) Modeling of swelling by the fast transient fluorescence technique in a polymeric gel. J Polym Sci B 38:739–746
16. Tari O, Pekcan O (2007) Swelling activation energy of κ-carrageenan in its gel state: a fluorescence study. J Appl Polym Sci 106:4164–4168
17. Pekcan O, Kaya D, Erdogan M (2000) Fast transient fluorescence (FTRF) technique to study swelling of densely and loosely formed gels. J Appl Polym Sci 76:1494–1502
18. Erdogan M, Pekcan O (2003) Swelling of heterogels in good solvents; a fast transient fluorescence study. Polymer 44:2129–2136
19. Pekcan O, Erdogan M (2003) Drying of heterogels swollen in organic vapor. Compos Interfaces 10:547–566
20. Enscore DJ, Hopfenberg HB, Stannett VT (1977) Effect of particle size on mechanism controlling normal-hexane sorption in glassy polystrene microsphere. Polymer 18:793–800