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Swelling of iota-carrageenan gels prepared with various $CaCl_2$ content: A fluorescence study

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Abstract: Iota carrageenan gels prepared with various $CaCl_2$ content were completely dried and then swelled in water vapor. Steady-state fluorescence (SSF) technique was used to monitor the swelling process of each iota carrageenan gels at various temperatures. Pyranine was used as a fluorescence probe. Apparent fluorescence intensity, *I* increased as swelling time increased for all gel samples. The increase in *I* was modelled using Li-Tanaka equation from which the swelling time constants, τ_1 and cooperative diffusion coefficients, D_c were determined. It was observed that D_c increased as the swelling temperature was increased. On the other hand at each temperature, it was seen that D_c decreased as $CaCl_2$ content was increased. Activation energies for swelling were obtained and found to be 60.5, 61.0, 61.5 and 62.8 $kJmol^{-1}$ for the gels prepared with increasing amount of $CaCl_2$ content.

Introduction

Carrageenan is obtained by water extraction after alkaline pretreatment from various species of red algae. It constituted of substituted and non substituted D-galactan units, linked by alternating α-1, 3 and β-1, 4 glucosidic bonds to a linear chain. The monomer units are partially substituted by sulfate half-ester groups, preferentially in the 2- and 4-position. On precipitation of the aqueous extract, several carrageenan fractions can be isolated, differing in degree of sulfation and content of 3,6-anhydride bridges within the galactose units. These fractions, represented commercial products and denoted as κ-, ι- and λ-carrageenan [1].

Iota carrageenan is the most highly sulphated of the helix-forming polysaccharides and is also the most fully characterized in the solid state and in solution [2]. This type of carrageenan is extensively used as gelling agent in food and pharmaceutical formulations. It is well known that iota carrageenan forms a three dimensional network constituted of polysaccharide chains structured as double helices. This gelation is induced by cooling heated suspensions of the polysaccharide in water under appropriate salt conditions resulting in a coil-helix conformational transition [2, 3]. It has been known that in solution, ι-carrageenan can reversibly transform from an ordered to a disordered conformation. Naturally at high ionic strength and low temperature ι-carrageenan forms an ordered state. On heating, the helices dissolve and the ι-carrageenan forms a random coil conformation [4]. Intermolecular double helix formation should result in a doubling in the observed molecular weight of the ι-carrageenan, which has been observed in many groups [2, 5]. However some

authors have proposed monomolecular single-helix formations [6]. It has been concluded that the formation of the ι-carrageenan double-helix follows second order reaction kinetics while the back reaction is a first order process. It has been shown that decrease in polymer concentration causes the change in the mechanism of ι-carrageenan conformational ordering from an intermolecular to an intramolecular multi-strand state [7].

The swelling and diffusion kinetics of physical gels are important in many technological applications. In pharmaceutical industries, in designing controlled release of drugs and in using cosmetic ingredients, understanding the kinetic of gel swelling 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. Many different experimental techniques have been used to study the kinetics of swelling and shrinking of chemical and physical gels such as neutron scattering [8], quasielastic light-scattering [9], macroscopic experiments [10] and in situ interferometric [11] measurements. The steady-state fluorescence technique was used for studying drying and swelling kinetics in disc shape gels [12-14]. Modeling of swelling by using fast transient fluorescence (FTRF) technique was reported [15]. Photon transmission technique was employed to study swelling and drying of polyacrylamide (PAAm) gels [16, 17]. Also photon transmission technique was used to study cation effect on thermal transition of carrageenans [18,19]. Conformational ordering of ι-carrageenan in $CaCl_2$ solution was also studied by using same technique [20]. The diffusion phenomenon of an aromatic molecule in ι-carrageenan gels was studied by the NMR spectroscopy [21].

In this work the effect of $CaCl_2$ content on the swelling process of iota carrageenan gels was investigated by using steady state fluorescence technique. Swelling of iota carrageenan gels was performed in water vapor. Pyranine was used as a fluorescence probe. It is observed that the apparent fluorescence intensity of pyranine increased during swelling process. Li Tanaka equation was employed to produce the swelling time constants, τ_1 and cooperative diffusion coefficients, D_c. The activation energies were determined for each gel by using Arrhenius relation.

Theoretical Considerations

The equation for swelling and shrinking of a gel disk as expressed by Li and Tanaka [22] is given by

$$\frac{u(r,t)}{u(r,0)} = \sum_n B_n \exp\left(-t/\tau_n\right) \tag{1}$$

where t denotes the time and $u(r, t)$ is the displacement vector of a point in the network from its final equilibrium location after the gel is fully swollen. The displacement vector is expressed as decomposition into components, each of them decaying exponentially with a time constant τ_n. The first term of the expansion is dominant at large t, that is, at the last stage of swelling. Eq. (1) can also be written in terms of solvent uptakes W and W_∞ at time t and at equilibrium, respectively, as follows

$$\frac{W_\infty - W}{W_\infty} = \sum_{n=1}^{\infty} B_n \exp\left(-t/\tau_n\right) \tag{2}$$

In the limit of large t or if τ_1 is much greater than the rest of τ_n, all higher terms $(n \geq 2)$ in Eq. (2) can be omitted, so that the swelling kinetic can be given by the following relation:

$$\left(1 - \frac{W}{W_\infty}\right) = B_1 \exp\left(-t / \tau_1\right) \tag{3}$$

Here B_1 is related to the ratio of the shear modulus, G, and the longitudinal osmotic modulus, $M = (K + 4G/3)$. Once the value of B_1 is obtained, one can determine the value of $R = G/M$, because the dependence of B_1 and R for a disk can be found in the ref. [22]. τ_1 is related to the collective cooperative diffusion coefficient D_c of a gel disk as

$$D_c = \frac{3a_\infty^2}{\tau_1 \alpha_1^2} \tag{4}$$

where α_1 is a function of R only (given in the ref. [23]) and a_∞ is the half thickness of the gel in the final equilibrium state. Once the quantities τ_1 and B_1 are obtained, R, α_1, and D_c can be calculated. Figure 1 shows the dependence of B_1 on R for disk-shaped gels [22].

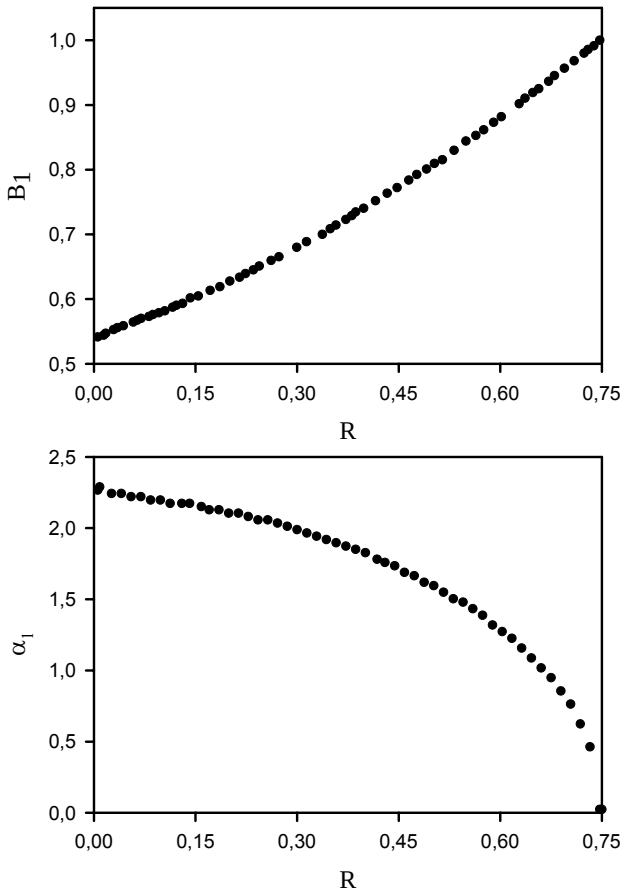

Fig. 1. The relationships between $B_1 - R$ and $\alpha_1 - R$.

Results and Discussion

Apparent fluorescence, I and scattered light, I_{sc} intensities monitored by using steady state fluorescence technique, against swelling times, t_s for the 2I1Ca gel swelled at 30 and 50 ^{o}C are shown in Figures 2a, b and 3a, b, respectively. It can be seen in Figures 2 and 3 that as scattered light intensity, I_{sc} decreased, fluorescence intensity increased during swelling. In fact, during swelling the transmitted light intensity, $I_{tr} = 1 - I_{sc}$ increased and the gel became more transparent; as a result I increases.

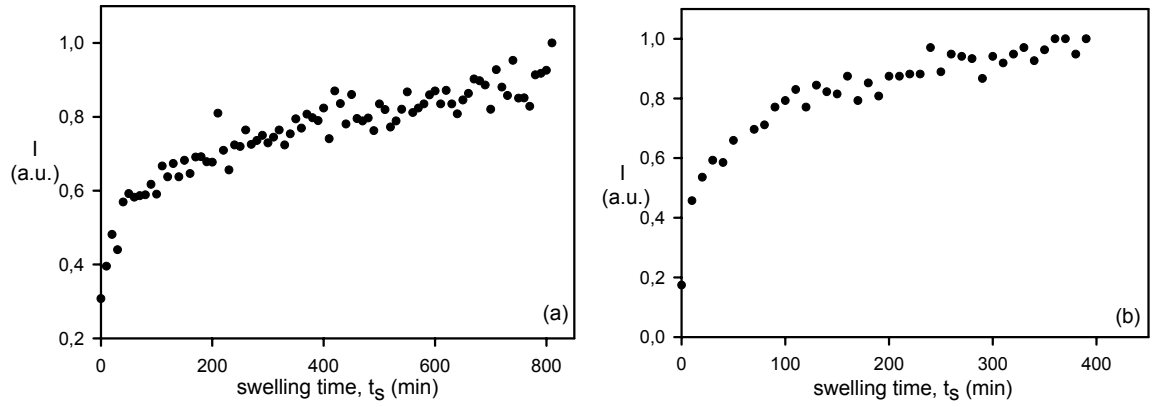

Fig. 2. Apparent fluorescence intensities of pyranine, I versus swelling time at a) 30 ^{o}C and b) 50 ^{o}C.

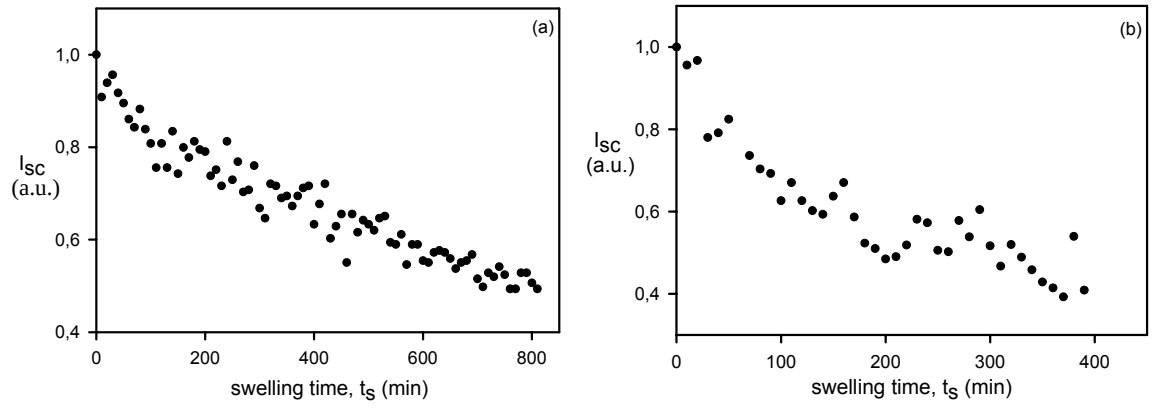

Fig. 3. Scattered light intensities of pyranine, I_{sc} versus swelling time at a) 30 ^{o}C and b) 50 ^{o}C.

Since swelling occurs in the gel state of carrageenan, one has to assume that pyranine molecules are embedded in the helices, so that no quenching of fluorescence can take place. In this sense no decrease can be expected in fluorescence intensity due to quenching. Decrease in turbidity originating from the dilution of helices and/or double helices, solely caused the increase in fluorescence intensity during swelling. This behavior can be understood by comparing Figure 2 with Figure 4. Except at early times almost one-to-one correspondence of fluorescence and transmitted light intensities can be seen. This picture confirms that increase in fluorescence intensity mostly come from the increase in transparency of carragenan gel during swelling. Early time behavior can be explained with the delay of gel transparency at which surface pyranines dominate the fluorescence intensity.

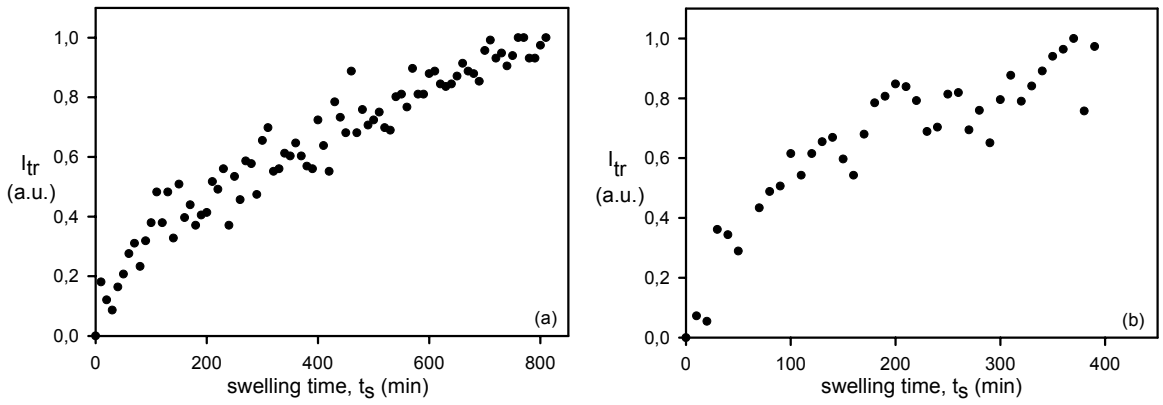

Fig. 4. Transmitted light intensities of pyranine, I_{tr} versus swelling time at a) 30 ^{o}C and b) 50 ^{o}C.

On the other hand, gel thickness in the direction of incident light increase more than the gel radius which keeps the number of pyranines constant in the incident light cone, then the effect of the dilution of pyranines to the fluorescence Intensity is negligible and can be omitted. In fact Li-Tanaka model considers only the gel thickness to calculate Cooperative Diffusion coefficient (see Eq. 4), which is in accord with our observations and assumption.

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

$$\frac{W}{W_\infty} = \frac{I}{I_\infty} \tag{5}$$

This relation predicts that as W increases, I increase. Combining Eq. (5) with Eq. (3) and calculating the logarithm of them, the following relation can be obtained

$$ln\left(1-\frac{I}{I_\infty}\right) = ln\,B_1 - \frac{t_s}{\tau_1} \tag{6}$$

where $t = t_s$ is taken in Eq. (3) to present the swelling time in Eq. (6).

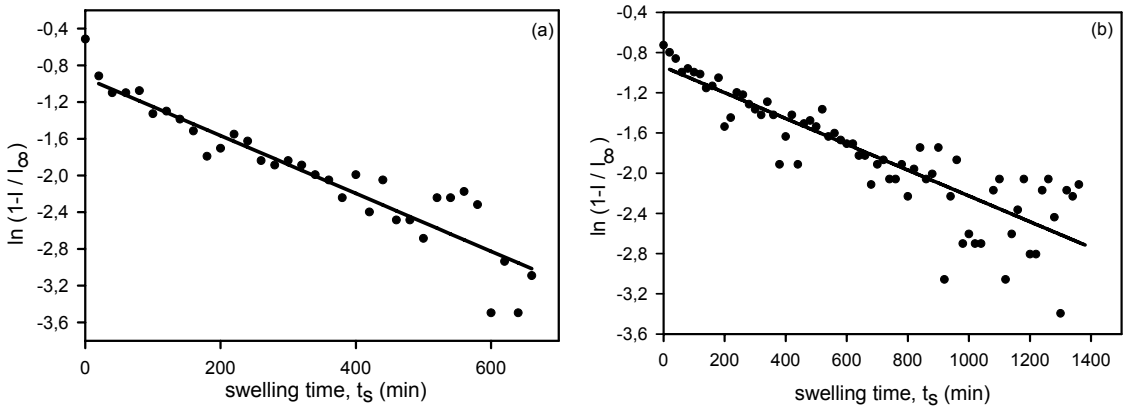

Fig. 5. Logarithmic plots of normalized I, according to Eq. (6) for 2I1Ca swelling in water vapor at a) 30^{o}C and b) 50^{o}C.

The data in Figure 2 are plotted in Figure 5 according to Eq. (6) where nice linear relations are obtained. Linear regression of curves in Figure 4 produces B_1 and τ_1 values from Eq. (6). Taking into account the dependence of B_1 and R, one obtains R values and from α_1 - R dependence, α_1 values were produced [22] (see Figure 1). Then using Eq. (4) cooperative diffusion coefficients D_c were determined and listed in Table 1 for various temperatures. The behavior of D_c versus temperature predicts that gel segments move much faster at higher temperatures during vapor penetration as expected.

Tab. 1. Experimentally determined swelling parameters for 2I1Ca gel swollen in water vapor at various temperatures.

Gel properties	Temperature			
	30°C	40°C	50°C	60°C
a_i (mm)	0,35	0,4	0,4	0,35
a_∞ (mm)	1,1	1	1,1	1,15
m_i (g)	0,0048	0,0057	0,0042	0,0023
m_∞ (g)	0,0298	0,0289	0,0279	0,0434
τ_1 (min)	525	243	143	67
$D_c x10^{-7}$ (cm^2/s)	0,55	1,01	2,16	4,97

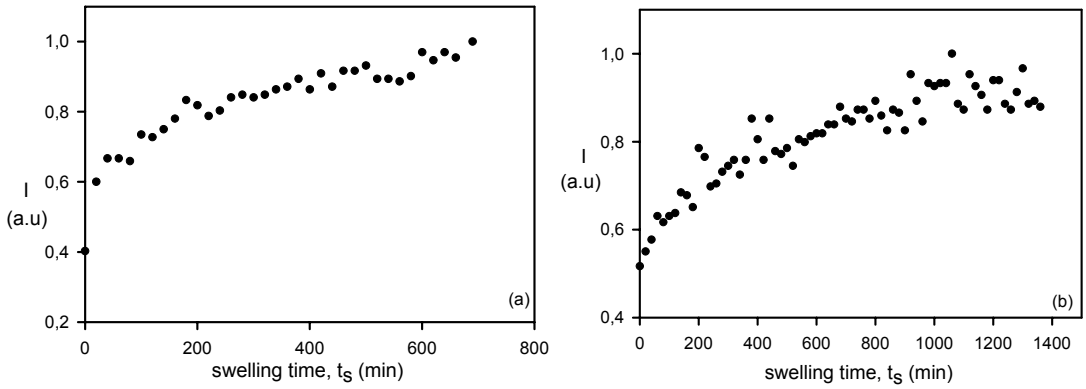

Fig. 6. Apparent fluorescence intensities of pyranine, I versus swelling time at 30°C for a) 2I08Ca and b) 2I12Ca.

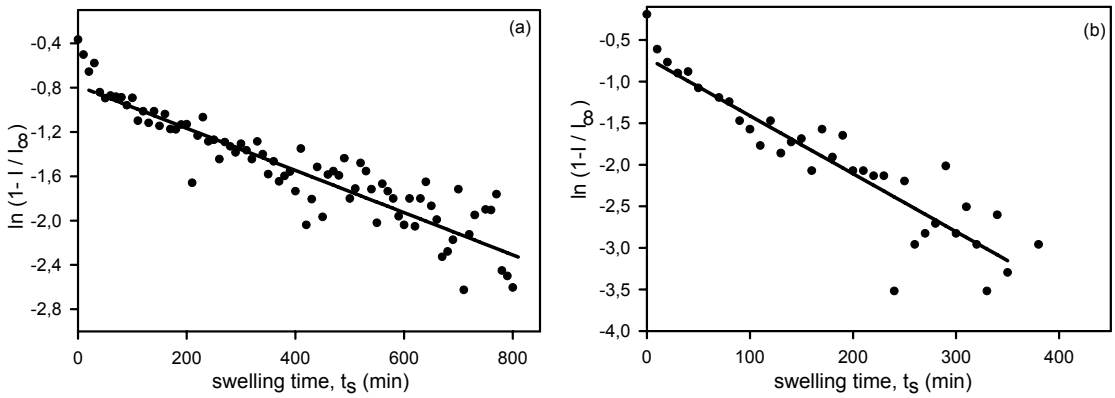

Fig. 7. Logarithmic plots of normalized I, according to Eq. (6) at 30°C for a) 2I08Ca and b) 2I12Ca gels swelling in water vapor.

The plots of apparent fluorescence intensity, *I* versus time during swelling of 2I08Ca and 2I12Ca are presented in Figures 6a and b at 30 ^{o}C, respectively. Using the Li-Tanaka model, cooperative diffusion coefficients, D_c were determined from the logarithmic plots of (1-(I / I_∞)) against t_s which are presented in Figure 7a and b for 2I08Ca and 2I12Ca samples respectively.

Tab. 2. Experimentally determined swelling parameters of the gels prepared in various $CaCl_2$ content in water vapor at 30 ^{o}C.

Gel properties	$CaCl_2$ content (wt%)			
	0,6	0,8	1,0	1,2
	2I06Ca	2I08Ca	2I1Ca	2I12Ca
a_i(mm)	0,35	0,45	0,35	0,45
a_∞ (mm)	1,15	1,15	1,1	1,1
m_i (g)	0,0056	0,0046	0,0048	0,0066
m_∞ (g)	0,0254	0,0199	0,0298	0,0296
τ_1 (min)	193	317	525	747
$D_c x10^{-7}$ (cm^2/s)	1,64	1,1	0,55	0,43

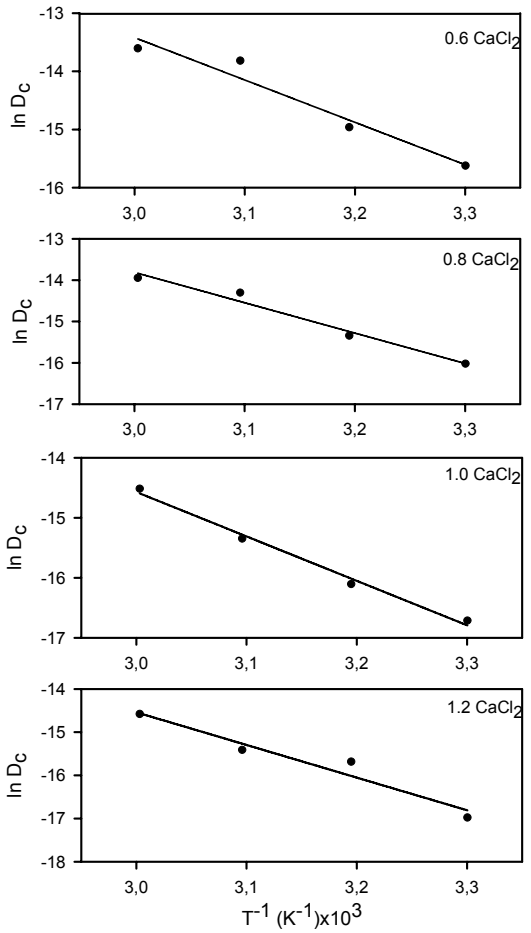

Fig. 8. The logarithmic plots of D_c values versus temperature T^{-1} according to Eq. (7). The slopes of the linear relation produce the activation energies ΔE for swelling process.

Experimentally produced D_c values for the gels prepared at various $CaCl_2$ contents are presented in Table 2 where, D_c values for the low $CaCl_2$ content (loosely formed) gels are found to be larger than the high $CaCl_2$ content (densely formed) gels.

In Table 2, the concentration effect of $CaCl_2$ on the vapor uptake can be clearly observed. In other words, gel segments in loosely formed gel moves much faster than they do in densely formed gels during water penetration, because higher $CaCl_2$ content in dense gels create higher density of double helices due to ionic attraction, which ends up with no free space for the water molecules to penetrate.

As seen in Table 1, the D_c values increase as the temperature is increased, which indicate that D_c - T relation may obey the Arrhenius relation as follows,

$$D_c = D_{co}\, exp\left(-\Delta E / RT\right) \tag{7}$$

where the ΔE is named as the activation energy for swelling, R is the gas constant, T is the temperature and D_{co} is the diffusion coefficient at $T = \infty$. The logarithmic form of the D_c data are plotted versus T^{-1} in Figure 8, where the slope of the linear relation produces the activation energy, ΔE for the swelling gels of 2I06Ca, 2I08Ca, 2I1Ca and 2I12Ca as 60.5, 61.0, 61.5 and 62.8 $kJmol^{-1}$, respectively.

Conclusions

The results in this work have shown that the fluorescence method can be used to monitor swelling process of iota carrageenan gels in vapor. This novel technique was employed to measure the swelling time constants, τ_1 and the cooperative diffusion coefficients, D_c for various gel samples prepared in various $CaCl_2$ contents and at different temperatures. Li-Tanaka model was applied to measure these parameters. It has been understood that both temperature and concentration affect the swelling process. It was observed that D_c increased as the swelling temperature increased and decreased while the $CaCl_2$ content was increased. The cooperative diffusion coefficient, D_c was found to obey the Arrhenius relation from where the activation energies were obtained and found to be slightly depending on $CaCl_2$ content i.e. larger activation energies were found for higher $CaCl_2$ content gel samples.

Experimental

Materials and Method

ι-carrageenan (Sigma C-1138) at (2%wt) was used to prepare disc-shaped gels by dissolving the powder in various $CaCl_2$ content solutions. Pyranine concentration was taken as $4x10^{-4}$ M for all samples, which is low enough to ensure that any excitation transfer effects are negligible. The heated carrageenan solution at 80 ^oC was continuously stirred by a magnetic stirrer and then poured into syringe and cooled to room temperature. These gels were dried at 30, 40, 50 and 60 ^oC for the swelling experiments respectively.

Swelling experiments were carried out for the gels prepared with various $CaCl_2$ contents from 0,6 to 1,2% (wt) at the same temperatures as they were dried, namely at 30, 40, 50 and 60 ^oC. These samples are named as 2I06Ca, 2I08Ca, 2I1Ca and 2I12Ca, respectively. Gel properties and experimental parameters are given in Table 1 and 2 where a_i and a_∞ are the thickness and m_i and m_∞ are the weights of the gels before and after the swelling process, respectively.

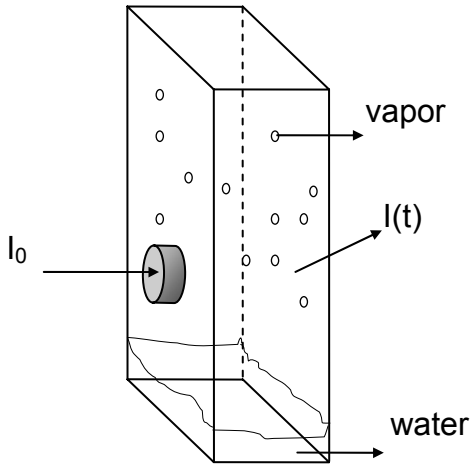

Fig. 9. The position of ι-carrageenan gel in fluorescence cell, during swelling in water vapor. I_o is the excitation and *I(t)* is the emission intensities at 460 nm and 515 nm, respectively.

At each temperature, the disc-shaped gel samples were placed on the wall of 1x1 quartz cell saturated with water vapor. The position of the gel, the level of water and the incident light beam, I_0 for the fluorescence measurements are shown in Figure 9. Perkin Elmer LS 50 model spectrometer, equipped with temperature controller was used for fluorescence studies. Pyranine in the carrageenan gels were excited at 460 nm and emission was detected at 515 nm as a function of swelling time at various temperatures. Typical fluorescence spectra from pyranine during swelling are presented at different swelling times in Figure 10. No spectral shift was observed during swelling experiments.

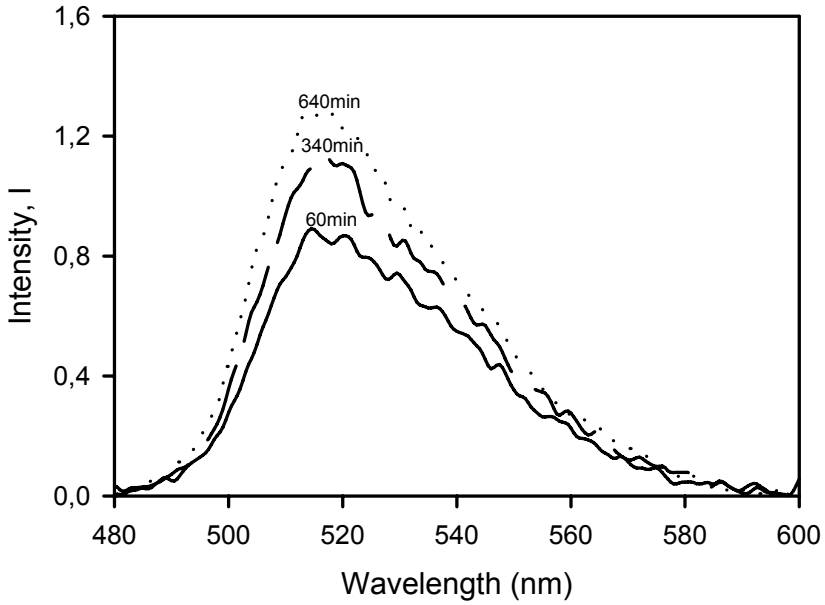

Fig. 10. Apparent fluorescence emission spectra of pyranine at different swelling times.

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