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Short communication

Crosslinking kinetics of cation-hydrocolloid gels

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Abstract

The gel formation of hydrocolloid (sodium alginate and kappa-carrageenan) is the result of the molecule aggregation in presence of an effective cation. The gelling process was considered as a process of diffusion–reaction between the effective cation and the hydrocolloid to produce a porous solid structure.

A simple mathematical model for predicting the reaction interface position in alginate or alginate-carrageenan gelation was developed. The model represents appropriately the physicochemical phenomenon and allows to determine the time for complete crosslinking of the hydrocolloid and the amount of incorporated ions.

Keywords: Alginate-carrageenan gel; Gelling mechanism; Model

1. Introduction

The hydrocolloids are natural carbohydrate polymers of high molecular weight used in the food industry for obtaining important functional properties, such as thickening, gel formation and texture stability. Pectin, gellan, agar–agar, kappa-carrageenan and sodium alginate are the most used hydrocolloids among the gelling agents accepted as additives in foods. Beside the application in the manufacture of modified foods, in the present they are used to produce particles for retention of enzymes, microorganisms or aromatic substances.

Alginates jellify and kappa-carrageenans form gels in a calcium- and a potassium-rich salt solution, respectively, producing hardening of the structure with shrinkage and repulsion of water [1].

The β-galactosidase is an enzyme used for the hydrolysis of lactose and is affected by cation concentrations. The enzyme activity is increased by potassium and reduced by calcium ions. Therefore, a mixture of those hydrocolloids is used in the β-galactosidase entrapment due to the synergistic behavior of both in the results, where K-kappa-carrageenan enhances the enzymatic reaction and Ca-alginate provides the appropriate mechanical strength [2]. The mechanical properties of these gels mainly due to alginate structure depend on the crosslinking of the three-dimensional networks formed and hence they are related to the kind and concentration of polymers and cations [3]. On the other hand, some undesirable effects of the mixture of these compounds should also be taken into account. High levels of calcium produce a chalky mouth-feel and may promote astringency or bitter taste in the product [4] or affect the enzyme activity [5]. Therefore, it is important to control concentration of cations.

The gelation reaction is produced when cations diffuse into hydrocolloid solution and specific segments of the alginate and carrageenan polymers interact with K^+ and Ca^{2+} ions getting the gel structure. For small solutes such as calcium and potassium ions and monosaccharides, the partition coefficient is equal to 1 [6].

Luh et al. [7] measured the thickness of the crosslinked region in pre-shaped soft gelatin slices as function of the immersion time and proposed a kinetics reaction that involved a linear relationship between those two variables. Experiments and photographs using cylindrical samples suggested that once the front has appeared due to the reaction, the crosslinking region could be easily divided from the unreacted region [7]. This front moves inwards the sample and it could indicate that a very fast reaction between the cations and unreacted substrate is taking place at the interface. Moreover, the solid structure that appears maintains its original shape and size.

Chavez et al. [9] used the amount of cation moles per volume unit of unreacted solid to explain the kinetics of

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Nomenclature

b	hydrocolloid stoichiometric coefficient (g hydrocolloid/g crosslinking agent)
C	concentration ($\mathrm{g\,cm^{-3}}$)
D_{eff}	effective diffusion coefficient of the crosslinking ion in the gel ($\mathrm{cm^2\,s^{-1}}$)
k_{l}	mass transfer coefficient in the liquid film ($\mathrm{cm\,s^{-1}}$)
r	radial coordinate (cm)
r_{c}	reaction interface position (variable with the time) (cm)
R	radius of the gelled cylinder (cm)
t	time (s)

Subscripts

0	inside the gelling bath
A	crosslinking cation
B	hydrocolloid

the gel formation, obtaining an expression that improves the calculation of the penetration thickness as function of the reaction time. However, the above-mentioned predictions of the penetration thickness did not agree well the experimental data as times increases.

Therefore, the objective of this work was to obtain a simple model for predicting the position of the moving reaction interface and for estimating the quantity of added cations at any time.

2. Theory

The gelling process was considered by Luh et al. [7,10], as a process of diffusion–reaction between the cation (A) and the hydrocolloid (B) to produce a porous solid gel (C). The crosslinking process can be described using a shrinking-core model. This model was developed for gas–solid reacting systems in which a nonporous solid B reacts with a gas A and a porous solid C is formed [11]. Explicit solutions were obtained for this reaction system in a cylinder of radius R and the following equations for the reaction interface position are obtained [12,13]:

$$r_{\mathrm{c}} = \sqrt{\frac{R^2((D_{\mathrm{eff}}/k_{\mathrm{l}}R) + (1/2)) - (2bD_{\mathrm{eff}}C_{A_0}t/C_B)}{(D_{\mathrm{eff}}/k_{\mathrm{l}}R) - \ln(r_{\mathrm{c}}/R) + (1/2)}} \qquad (1)$$

and

$$C_A = \frac{C_{A_0}}{(D_{\mathrm{eff}}/k_{\mathrm{l}}R\ln(r/r_{\mathrm{c}})) + (\ln(R/r)/\ln(r/r_{\mathrm{c}}))} \qquad (2)$$

where D_{eff} is the effective diffusion coefficient of cation A in the porous solid gel; k_{l} the mass transfer coefficient in the liquid film around the solid; C_{A_0} the concentration of cation A in the solution bulk; C_B the hydrocolloid concentration in the unreacted core; b the hydrocolloid stoichiometric coefficient (g hydrocolloid/g crosslinking agent); and r_{c} is the reaction interface radial position.

For short reaction times, when $[\ln(r_{\mathrm{c}}/R)]$ values are negligible, an approximate equation can be obtained from Eq. (1):

$$\frac{R^2 - r_{\mathrm{c}}^2}{R^2} = \frac{2bD_{\mathrm{eff}}C_{A_0}t}{C_BR^2((D_{\mathrm{eff}}/k_{\mathrm{l}}R) + (1/2))} \qquad (3)$$

Moreover, when reaction is starting ($r_{\mathrm{c}} \rightarrow R$), a new approximated equation can be obtained from Eq. (1) for very short reaction times:

$$\frac{R - r_{\mathrm{c}}}{R} = \sqrt{\frac{2bD_{\mathrm{eff}}C_{A_0}}{C_BR^2((D_{\mathrm{eff}}/k_{\mathrm{l}}R) + (1/2))}}\sqrt{t} \qquad (4)$$

Eq. (4) is a relationship between the interface position and the time similar to those proposed by Ak et al. [8] and Chavez et al. [9]:

$$\frac{R - r_{\mathrm{c}}}{R} = k'\sqrt{t} \qquad (5)$$

where $(R-r_{\mathrm{c}})/R$ is the dimensionless penetration thickness.

The complete gelation time of the hydrocolloid (t_{g}) can be calculated when $r_{\mathrm{c}} \rightarrow 0$ in Eq. (1), resulting

$$t_{\mathrm{g}} = \frac{C_BR^2}{2bD_{\mathrm{eff}}C_{A_0}}\left(\frac{D_{\mathrm{eff}}}{k_{\mathrm{l}}R} + \frac{1}{2}\right) \qquad (6)$$

3. Materials and methods

Solutions of commercial sodium alginate (Kelgin LV from Kelco, Chicago) of 2.4% (w/v) and solutions of sodium alginate and commercial kappa-carrageenan (Gelacid C-3 from Biotec SA, Buenos Aires, Argentina) of 2.4 and 1.0% (w/v), respectively, were used for preparing different gel samples. Cylindrical samples (11.04 mm diameter and approximately 120 mm height) were obtained using a membrane for dialysis of 1000 nominal molecular weight cut-off (MWCO) held by support.

The cylinders containing the sodium alginate solution were immersed in different flask provided with agitation, at room temperature (approximately 25 °C), containing 500 ml of $\mathrm{CaCl_2}$ solutions of 1.0, 2.0 or 3.0% (w/v) each. Analogous procedure was carried out with the alginate-carrageenan solutions, which were immersed into $\mathrm{CaCl_2}$:KCl solutions of 1:2, 2:4 and 3:6% (w/v). All the used salts were of analytic quality or better (Mallinckrodt, St. Louis).

The gelled samples were removed at different times and cut to obtain a central cylinder of 1.104 cm diameter and approximately 1.0 cm height. Each sample was washed with distilled water to remove the unreacted region. The solid crosslinked layer was easily visualized due to its hardness. The thickness of penetration was measured using a calliper (Mitutoyo model), with 0.002 cm of precision. Each assay was carried out in duplicate.

Ca and K concentrations were determined in the gel and in the gelling bath before and after immersion of cylindrical samples by an atomic absorption spectrophotometer (5000 Perkin-Elmer model) according to the method proposed by the Operation Manual Perkin-Elmer—Atomic Absorption Cooking Book [14].

4. Results and discussion

The hydrocolloid gelling reaction is a function of the reactant agents and its concentration. When hydrocolloid solution contacts cation solution, gel is formed immediately at the interface. Further gelation depends on cation diffusion through the gelled layer and varies with the time until the unreacted zone disappears. The cation-hydrocolloid interactions forming a solid structure as the cation is gradually uptaken, result in a gradual strengthening of the gel [1]. The cation concentration values experimentally obtained for the different concentrations used determine the stoichiometric coefficient (b). In the calcium alginate gelation, the value of coefficient b was 24.26 g of the used sodium alginate per gram of calcium, being b the minimum amount of cations necessary for gel formation.

Experimental values of the average cation concentration (Ca and K) incorporated by chemical reaction to the gel structure, obtained by gelation of a 2.4% (w/v) sodium alginate and 1.0% (w/v) kappa-carrageenan solution for different gelling bath compositions are shown in Table 1. As it is observed, the incorporation of cations into the gel structure increases with the immersion time. Also, the gel strength usually increases with time due to structural rearranges produced by the bridge of hydrogen bonds [3].

Due to cations complete polymer reactive groups and also saturated the solution in the solid, the highest calcium concentration reached is slightly higher than theoretical one for complete chemical reaction, which is related to the $1/b$ value.

Once the hydrocolloid and cation solutions have been mixed, is essentially impossible to stop the interaction. The reaction will continue until equilibrium is reached. The hydrocolloid gels produced by interaction with cations are dynamic systems.

To validate the theoretical model, values of D_{eff} and k_{l} are necessary. Due the gelation assays were carried out into a magnetic agitated vessel, the external mass transfer effect not affect substantially the determination of penetration thickness. For this reason, the $[D_{\mathrm{eff}}/(k_{\mathrm{l}}R)]$ term was neglected.

The diffusivity of calcium chloride at infinite dilution in water at 25 °C is $D_{\mathrm{CaCl_2}} = 13.35 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$ [15]. The diffusion constant for the diffusion–reaction model is expected to be smaller than the literature value for infinitely diluted solution, mainly due to the sterical hindrance of the random movement of the ions by the gel matrix [16]. A reduction of 37% of the D_{eff} value was obtained by magnetic resonance imaging for the calcium ion when 2.0% (w/v) sodium alginate solution is crosslinked with 9.0% (w/v) calcium dichloride solution [17] and the values of 1.799×10^{-6} and $1.673 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$ were obtained for gelatin-alginate and agar-alginate gels, respectively [9].

Using experimental values for penetration thickness at different times, a D_{eff} value of 5.33×10^{-6} and $1.80 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$ were obtained with Eqs. (3) and (4), respectively; although using Eq. (3) a non-linear approach diffusivity values for each pair of experimental results were changing, giving higher values ($9.63 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$) at the beginning of the gelation. The value obtained experimentally was considered as a reasonable result and was used as an average for the penetration thickness.

A good agreement between experimental and theoretical data of thickness of penetration in a sodium alginate as function of time predicted with Eq. (1), are shown in Table 2.

The rate of the penetration thickness for sodium alginate or sodium alginate and kappa-carrageenan mixture was similar, since the values obtained were equals for both solutions. This could be explained by considering that crosslinking reactions in the alginate are responsible of the gel structure and the quantity of carrageenan did not affect the structure.

The experimental times for complete gelation with the used conditions were approximately 11700, 5880 and 3900 s for $CaCl_2$ solutions of 1, 2 and 3%, respectively. Eq. (6) predicts t_g values of 11605, 5802 and 3868 s, representing an error less than 1%. This error value is lower than values obtained using the equations proposed by Ak et al. [8] and Chavez et al. [9] due that these only are considered more

Table 1
Amount of cations into gel obtained from a 2.4% (w/v) sodium alginate and 1.0% kappa-carrageenan solution gelling with different bath concentration

Immersion time (s)	Gelling bath 1.0% $CaCl_2$–2.0% KCl		Gelling bath 2.0% $CaCl_2$–4.0% KCl	
	Ca[a] ($10^{-3}\,\mathrm{g\,cm^{-3}}$)	K[a] ($10^{-3}\,\mathrm{g\,cm^{-3}}$)	Ca[a] ($10^{-3}\,\mathrm{g\,cm^{-3}}$)	K[a] ($10^{-3}\,\mathrm{g\,cm^{-3}}$)
1800	0.143	0.249	0.188	0.321
3600	0.190	0.269	0.245	0.347
5400	0.205	0.321	0.265	0.366
7200	0.245	0.344	0.280	0.367
9000	0.263	0.367	0.282	0.367
10800	0.280	0.367	0.284	0.367
12600	0.282	0.367	0.284	0.369

[a] Error range: ±0.001.

Table 2
Advance of gelation interface in sodium alginate for 1.0, 2.0 and 3.0% (w/v) $CaCl_2$ gelling bath

Immersion time (s)	r_c (cm)					
	1.0% $CaCl_2$		2.0% $CaCl_2$		3.0% $CaCl_2$	
	Measured[a]	Calculated	Measured[a]	Calculated	Measured[a]	Calculated
0	0.552	0.552	0.552	0.552	0.552	0.552
300	0.496	0.490	0.468	0.462	0.448	0.440
600	0.466	0.462	0.428	0.422	0.388	0.390
900	0.440	0.440	0.376	0.389	0.350	0.350
1800	0.386	0.390	0.318	0.315	0.250	0.252
2700	0.350	0.350	0.248	0.251	0.162	0.164
3600	0.312	0.314	0.180	0.193	0.064	0.063
3900	–	–	–	–	0.000	[b]
4500	0.284	0.282	0.124	0.133		
5400	0.250	0.251	0.072	0.063		
5880	–	–	0.000	[c]		
6300	0.226	0.222				
7200	0.190	0.193				
8100	0.166	0.164				
9000	0.134	0.134				
9900	0.104	0.101				
10800	0.066	0.063				
11700	0.000	[d]				

[a] Error range: ±0.002.
[b] The theoretical time to complete the gelation was 3868 s.
[c] The theoretical time to complete the gelation was 5802 s.
[d] The theoretical time to complete the gelation was 11605 s.

simplified models presenting a linear adjustment for larger times where errors increased for variable simplification.

Fig. 1 shows the experimental data and theoretical values predicted with Eqs. (1) and (4) for the solid interface position at different times in the alginate and alginate-carrageenan matrices gelling with $CaCl_2$ (2%) and $CaCl_2$:KCl (2:4%). The better adjustment of Eq. (1) was more appreciable at longer immersion times. The k' constant obtained with Eq. (4) after the substitution of variables by corresponding values, was $0.01313\,s^{-1/2}$, which was similar to the one obtained by the regression of the experimental data, $0.01311\,s^{-1/2}$.

Eq. (2) allows calculating the theoretical available Ca^{2+} cations inside the gel as it is shown in Fig. 2. Moreover, the reaction interface position of a 2.4% (w/v) sodium alginate solution can be observed when Ca^{2+} concentration reaches

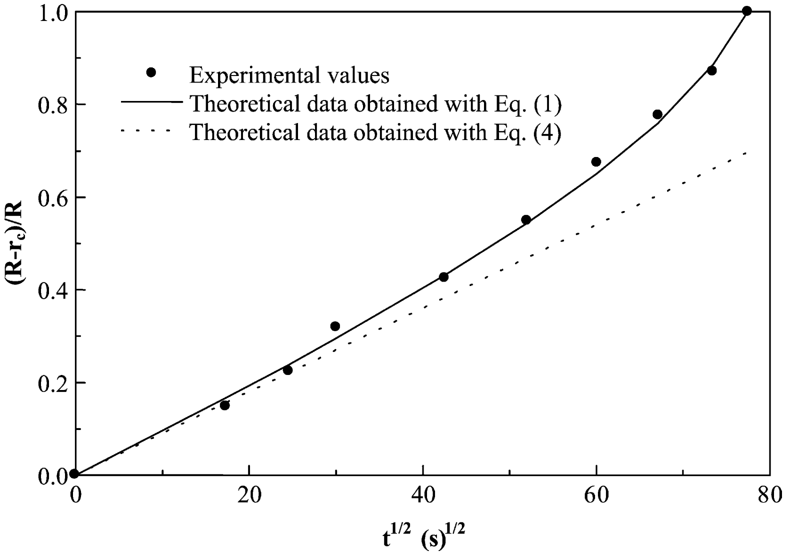

Fig. 1. Theoretical and experimental data for penetration thickness of calcium into a sodium alginate gel for a 2.0% (w/v) $CaCl_2$ gelling bath.

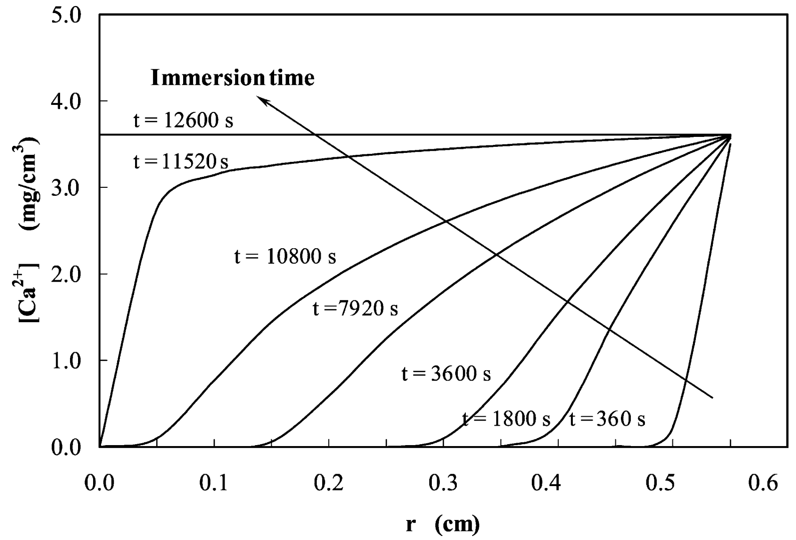

Fig. 2. Calcium cation profiles inside a sodium alginate gel obtained in a 1.0% (w/v) $CaCl_2$ gelling bath.

a zero value for each immersion time. These data are particularly important in enzyme immobilization to calculate the immersion time that ensures the required structural characteristics in a catalyst without over-exposing the enzyme to the inhibitor effect of the Ca^{2+} cations.

5. Conclusions

The shrinking-core model allows predicting appropriately the hydrocolloid gelation process. Through this model, the position of the gelation front and the amount of incorporated ions at a determined time can be estimated.

Explicit approaches of the constant that relates penetration thickness and time can be used to determine the modification of variables involved in the gelling process.

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