ELSEVIER

Carbohydrate Polymers 51 (2003) 125–134

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

A novel method for measuring hydration and dissolution kinetics of alginate powders

Christian Klein Larsen[a], Olav Gåserød[a,*], Olav Smidsrød[b]

[a]*FMC BioPolymer, Tomtegt 36, N-3002 Drammen, Norway*

[b]*Norwegian Biopolymer Laboratory (NOBIPOL), Department of Biotechnology, Norwegian University of Science and Technology, N-7491 Trondheim, Norway*

Received 30 November 2001; revised 10 January 2002; accepted 28 January 2002

Abstract

A novel method was developed to determine hydration and dissolution kinetics for well dispersed alginate powders added to agitated water. A special propeller and a StressTech rheometer were used to monitor the increase in viscosity as function of time. The shear stress values obtained from the rheometer were used as a parameter for the viscosity, and relative dissolution curves were plotted using shear stress/alginate concentration standard curves, or directly using the shear stress values as a parameter for dissolved alginate. These curves were fitted to an exponential function that gave the rate constant for the dissolution process, and a time constant related to the time necessary to hydrate the alginate particles. The standard curves were linear between the logarithm of the shear stress and the alginate concentration above 0.1% (w/v).

The alginate powders were usually dispersed in sugar. For particle size 250 μm, an alginate/sugar ratio of 1:5 was found sufficient for good dispersion. Increased particle size led to a decrease in the dissolution rate, while raising the stirrer speed increased dissolution rates. The rate constant increased with increased temperature as given by Arrhenius' law, and the activation energy for dissolution in water was found to be 23 kJ/mol, suggesting that diffusion of alginate from the particle to the surrounding solution was the rate determining step in the dissolution process. Further evidence for this was obtained by comparing the dissolution rate in solution of non-gelling ions (Na^+, K^+ and Mg^{2+}) at different ionic strengths. The decreased rate at higher ionic strength and in particular the lower dissolution rates in excess of the divalent Mg^{2+}-ion could well be accounted for, in a qualitative manner, by the Nernst–Hartley equation for diffusion of polyelectrolytes.

With Ca^{2+}-salts in the solvent, partly hydrated particles were formed giving viscosity values going through a maximum above a critical Ca^{2+}-concentration. The presence of a non-ionic polymer, polyethylene glycol, resulted in a decrease in the dissolution rate.

Keywords: Alginate; Dissolution rate; Hydrocolloid hydration

1. Introduction

Alginates are usually delivered by the producer as powders, and as for hydrocolloids in general, some common problems are connected to their dissolution. Alginate has high affinity for water and tends to stick to the stirrer device and form lumps when dissolved in water. This gives prolonged dissolution times and thus increased processing time and cost for the industry. More knowledge about the dissolution mechanisms and lump-forming tendency can make alginate applications more effective. Also, in applications where water availability is limited or where gelling ions and sequestrants are acting in a given time frame, the control of hydration kinetics becomes crucial for utilizing the entire functionality of the alginate.

Little scientific research has been done in the field of measuring and quantifying hydration and dissolution rates for hydrocolloids. To, Mitchell, Hill, Bardon, and Matthews (1994) showed that the viscosity development could be represented by an exponential function, and further that the hydration rate became independent of a given mixer speed above 3000 rpm. More recently Kravtchenko, Renoir, Parker, and Brigand (1999) have developed a simple method for determination of the dissolution rate for hydrocolloid powders, using pectin as testing material. By agitating the solvent in a vessel with a special propeller, they measured the viscosity development after adding pectin by sampling the torque applied to the stirrer. The measured values for torque was correlated to pectin concentrations

---

* Corresponding author. Tel.: +47-3220-3564; fax: +47-3220-3510.
E-mail address: olav_gaserod@fmc.com (O. Gåserød).

PII: S0144-8617(02)00139-X

through standard curves, and the dissolution curves were fitted to an exponential function.

Work has also been done to model the dissolution of spherical particles of non-ionic polymers (Devotta, Ambeskar, Mandhare, & Mashelkar, 1994; Ranade & Mashelkar, 1995). Devotta et al. (1994) assumed that the dissolution process could be divided into two steps; swelling and partly hydration, and the dissolution and disentanglement of the polymer chains. Ionic and non-ionic polymers are very different in nature, but this is a mechanism that can be assumed to apply also to alginate dissolution. Although diffusion driven, these two steps will experience two different controlling regimes, mainly water diffusion for the swelling process and water-, ion- and alginate diffusion for the disentanglement. Devotta et al. (1994) also found that for a polymeric particle, the dissolution rate became independent of particle size below a certain particle size limit.

In the case of alginate dissolution, it has also been proposed that the diffusion of the counter ions into the solvent leads to a dragging force on the polymer chains (Thu et al., 2000), a mechanism not applying to non-ionic polymers. Electroneutrality has to be maintained also locally, so the diffusion of the counter ions must be coupled with the large polyanionic chains.

Several attempts have been made to develop a theoretical rationale for the diffusibility of polyelectrolytes (Cantor & Schimmel, 1980; Hodgson & Amis, 1993; Tanford, 1961) and the diffusion constants will depend on a number of factors like the size and shape of the macromolecule, its charge and concentration and most important on the type of counterion and the ionic strength of the solution. In a polyelectrolyte solution the mutual interaction between small counterions and large polyions will slow down the rapid movement of small ions and speed up the movement of large polyions (Foster, Schmidt, & Antonietti, 1990; Lin, Lee, & Schurr, 1978). This interaction will be reduced when the ionic strength increases, and this effect explains in a qualitatively way the increase in the diffusion coefficient of a number of polyelectrolytes when the ionic strength is lowered.

Based on the diffusion theories in multicomponent systems (Cantor & Schimmel, 1980; Hodgson & Amis, 1993; Thu et al., 2000; Treml & Kohler, 2000), the following equation for the effective diffusion constant of sodium alginate in aqueous solution can be derived

$$D_{\mathrm{eff}} = (1+|Z_{\mathrm{Alg}}^{\mathrm{eff}}|)\frac{D_{\mathrm{Na}}D_{\mathrm{Alg}}}{D_{\mathrm{Na}} + \left|Z_{\mathrm{Alg}}^{\mathrm{eff}}\right|D_{\mathrm{Alg}}} \quad (1)$$

where $Z_{\mathrm{Alg}}^{\mathrm{eff}}$ is the effective valency of the negatively charged alginate molecule under the influence of counterion condensation (Manning, 1978), the numerical value $|Z_{\mathrm{Alg}}^{\mathrm{eff}}|$ then becoming the number of fully dissociated sodium ions per alginate molecule, D_{Na} and D_{Alg} are the diffusion coefficient for sodium ions and the alginate molecule, respectively, in dilute solutions without taking into account the electrostatic interactions. The equation, which may be seen as a special case of the Nernst–Hartley equation (Barthel, Krienke, & Kunz, 1998), shows that when $Z_{\mathrm{Alg}}^{\mathrm{eff}}$ is very large, D_{eff} approaches the value of the sodium diffusion coefficient, D_{Na}. However, at high ionic strength the electric force in the alginate molecule is greatly reduced and D_{eff} will approach the value D_{Alg} without electrostatic interactions. Several theoretical approaches have been attempted to give a quantitative description of this effect (Hodgson & Amis, 1993), but these will not be discussed here. In a hydrated alginate particle each alginate molecules must be surrounded by a large number of sodium ions which will tend to diffuse into the solution of lower concentration, and the alginate chains will experience an electrostatic force pulling the chains into solution with a rate governed by the factors given above. One object of the present work is to obtain experimental data for this hypothesis.

On the experimental side, our goal was to develop a rapid and reproducible method for measuring hydration kinetics using a standard rheometer equipped with cup and propeller providing shear rate sufficient to dissolve the alginate. At the same time it should measure the increasing shear stress as more alginate goes into solution. Dissolution processes in the industry usually include stirring at constant speed, and the measurements on the rheometer were therefore done at constant shear rate. To quantify the dissolution kinetics, the dissolution curves were fitted to a slightly modified model compared to the one used by Kravtchenko et al. (1999). This function avoids the necessity to include the point (0,0) as the first point, and gives a parameter that in some way represents the time delay that occurs as a result of hydration and swelling before the dissolution process starts. By introducing a time constant to the function, the rate constant can be calculated being less affected by differences in the procedure of adding the sample manually.

2. Experimental

2.1. Materials

The alginates used are given in Table 1, and the monomer composition of these is shown in Table 2. The chemical composition and sequence of the given alginates was determined by high-field NMR (Grasdalen, 1983). Intrinsic viscosity was determined in 0.1 M NaCl at 20 °C on a capillary viscometer (Lauda, D 15 KP), and viscosity in 1% solution was measured using a Brookfield RVT DV-III viscosimeter. To compare different alginate samples, the powders were sieved into similar particle size fractions on a Retsch Vibro sieving machine. Dispersion of the alginate powders was principally done in two ways; by manually mixing the powder with sugar on a parchment paper with a metal spatula, or by adding the alginate (0.15 g) to ethanol

Table 1
Chemical composition of alginates used

Alginate sample	Alginate description	Source	Viscosity 1% (mPa s)	Particle size (μm)	Molecular weight, M_w (g/mol)
1	Na-alginate	*Laminaria hyperborea*, stem	242	250	280,000
2	Na-alginate	*Laminaria hyperborea*, stem	672	250	362,487
3	Na-alginate	*Laminaria hyperborea*, stem	6.5	250	35,000
4	Na-alginate	*Laminaria hyperborea*, stem	40	250	147,000
5	Na-alginate with 1% viscosity 130 mPa s	*Laminaria hyperborea*, stem	130	190–250	
6	Na-alginate with 1% viscosity 414 mPa s	*Laminaria hyperborea*, stem	414	190–250	
7	Na-alginate with 1% viscosity 768 mPa s	*Laminaria hyperborea*, stem	768	190–250	
8	Na-alginate with 1% viscosity 1970 mPa s	*Laminaria hyperborea*, stem	1970	190–250	
9	K-alginate	*Laminaria hyperborea*, stem		125–180	
10	Mannuronan	*Pseudomonas*		<250	
11	Na-alginate	*Durvillea potatorum*	302	250	

(0.5 ml). Castor sugar, approx. 500 μm in diameter, was used as dispersing agent.

2.2. Measuring system

A StressTech rheometer was mounted with the propeller shown in Fig. 1. The cylindrical rheometer cup had the following dimensions: inner diameter 27 mm and depth 62 mm.

In an attempt to calibrate the propeller, despite the turbulent conditions, the shear stress constant for the propeller was roughly calculated to 200,000 m^{-3} after the equation (personal communication, Mads Larsson, Rheologica, Sweden, 2000)

$$k_{ss} = 1/2\pi L r^2 \tag{2}$$

where k_{ss} is the shear stress constant, L the blade height and r the radius in the circle formed by the rotating blades. The shear rate constant was then found by setting its value to 1, measure the viscosity on a standard calibration oil (49.8 mPa s, Brookfield), and adjusting the shear rate constant until the right viscosity was measured. When the rheometer was measuring at maximum speed, this constant was found to be 8.785 $\mathrm{s}^{-1}\,\mathrm{rad}^{-1}$. The maximum rotational speed at constant shear rate settings was measured to 703.5 rpm with a tachometer (Tach-IV, Monarch Instruments, USA), and the shear rate at this speed was given as 557.6 s^{-1}.

2.3. Addition of alginate samples and measurements

Dispersed samples of alginate powders (0.15 g alginate mixed with 1.35 g sugar for 1:10 dispersion and 1.0% final concentration) were added manually from a parchment paper directly into the rheometer cup. The solvent volume was 15 ml. The addition was usually done during a period of 2 s and roughly 10 s after starting the rheometer. Time zero was later set to the time of alginate addition, and the amount of dissolved alginate was at this point set to be zero.

Standard curves were obtained in the range 0.1% (w/v) and up to above 1.5% alginate solution by linear fitting to the function

$$\log \sigma = ac + b \tag{3}$$

where σ is the measured shear stress, a is the slope of the line, c is alginate concentration in % (w/v) and b is the y-axis intersection. The standard curves were obtained by measuring shear stress on alginate solutions with known concentration. When adding alginate dispersed in sugar, the sugar will in most situations be totally dissolved in 20 s (Kravtchenko et al., 1999). This was visually verified in a transparent plastic cylinder. Because of this, all the points in the standard curves had the same amount of sucrose dissolved (9% for 1:10 dispersion and 1% final alginate

Table 2
M- and G-content in used alginates where this is known

Alginate	F_G	F_M	F_{GG}	F_{MM}	$F_{GM,MG}$	F_{GGG}	F_{GGM}	F_{MGM}	$N_{G>1}$
Sample 1	0.69	0.31	0.54	0.16	0.15	0.5	0.04	0.09	15
Sample 2	0.662	0.338	0.54	0.216	0.122	0.49	0.05	0.072	11.8
Sample 3	0.73	0.27	0.61	0.15	0.12	0.58	0.028	0.09	23
Sample 4	0.71	0.29	0.55	0.14	0.16	0.5	0.05	0.1	11.57
Sample 10	0.0	1.0	0.0	1.0					
Sample 11	0.32	0.68	0.2	0.56	0.12	0.16	0.05	0.07	5.51
Generally for *Laminaria hyperborea*, stem[a]	0.68	0.32	0.56	0.20	0.12				

[a] Data from Moe, Draget, Skjåk-Bræk, and Smidsrød (1993).

Fig. 1. The propeller mounted to the rheometer used for agitating and measuring shear stress after adding alginate to the water. Made by Rheologica AB, Lund, Sweden. The propeller, positioned 6 mm above the bottom of the rheometer cup, had the following dimensions: length 99 mm, bar diameter 7.5 mm, vertical blade height 10 mm, blade angle approx. 48° and propeller diameter 18 mm.

concentration) to represent the measuring conditions. Longer dissolution time for sugar can be experienced at high levels of dry matter such as glycerol.

2.4. *Effects of dry matter content and polyethylene glycol (PEG) measurements*

Mixtures of glycerol and water were used for measurements at different levels of dry matter. The sugar used as dispersion agent was calculated as part of the total dry matter. The alginate concentration was approx. 0.28% (w/w).

Polyethylene glycol ($M_w = 35,000$) was used to investigate the effect of the presence of a low compatible compound in the solvent.

3. Results and discussion

3.1. *Method*

3.1.1. *Propeller calibration and necessary agitation speed*

A shear rate sweep at the rheometer revealed that the propeller calibration was invalid for all other shear rates than the calibration speed. This led to the use of shear stress values as viscosity parameter. Additionally, due to major turbulence in the solution, the rheometer measured false viscosity values at viscosity levels both higher and lower than the calibration viscosity.

To visually investigate the necessary agitation speed, a transparent plastic cup with the same dimensions as the rheometer cup was used with the rheometer propeller on a traditional agitator, making it possible to observe the development of a vortex. At 600–700 rpm a sufficient vortex was developed, and the propeller blades were still totally covered by the water.

3.1.2. *Standard curves*

Fig. 2 shows the standard curve for alginate sample 1 in 9% sucrose solution. The relation between logarithmic shear stress values and alginate concentration is linear in the range 0.1–1.0%. Since there was a non-linear trend for alginate concentrations less than 0.1%, the first measured points corresponding to concentrations less than 0.1% were not used in the curve fit model. Additionally, sugar takes approx. 20 s to dissolve, and the fitting model should only be applied for points after 20 s. In cases where the alginate dissolves within 20 s, the viscosity development will mainly be due to the alginate dissolution, and the sugar contribution is ignored.

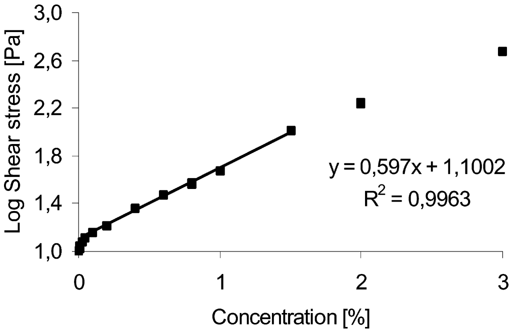

Fig. 2. Standard curve for Na-alginate (sample 1) in 9% sucrose solution. Shear stress values are logarithmically plotted against alginate concentration and linear fitted in the area 0.05–1.5% alginate concentration.

3.1.3. *Dissolution curves, calculation of dissolved amount of alginate and empirical data fitting*

Fig. 3 shows the measured shear stress values for sample 1 dispersed 1:10 in sugar. These values can be correlated to the alginate concentrations from the standard curve for the alginate (Eq. (3)):

$$c = 1/a(\log \sigma - b) \tag{4}$$

The calculated alginate concentrations can be given as percent dissolved by relating the values to the final concentration, and hence give relative dissolution curves ranging from 0 to 100% dissolved alginate

$$m = c/c_\infty 100\% \tag{5}$$

where m is the dissolved fraction of the sample (% of total amount) and c_∞ is the final concentration.

The finding of linear standard curves led to the conclusion that applying standard curves was not necessary for determining the dissolution rates. The measured shear stress values can be directly used to calculate relative values for dissolved alginate. To do this, it was necessary to measure the shear stress for the solvent containing the

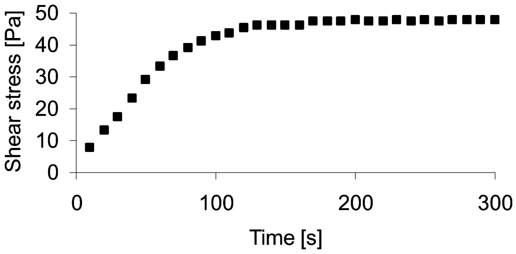

Fig. 3. Viscosity development, given as shear stress, measured by the rheometer after adding 1:10 sugar dispersed alginate (sample 1) to 1% concentration. Fig. 4 shows the dissolution curve after calculation of concentrations and fitting the data to Eq. (8).

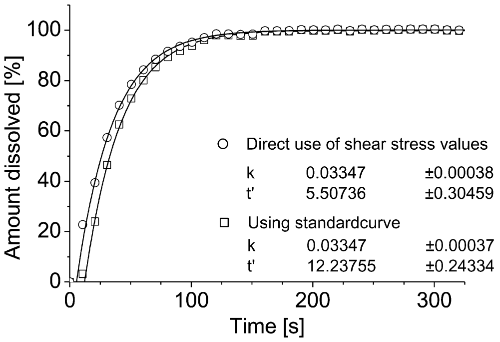

Fig. 4. Dissolution curves for sample 1 (1% solution, dispersed 1:10 in sugar) obtained from the data in Fig. 3 through a standard curve and direct use of the shear stress values. Values from 20 s are fitted to Eq. (8).

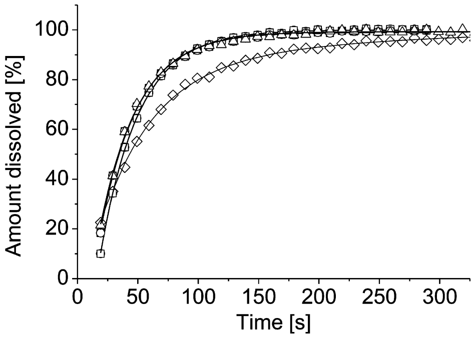

Fig. 6. Dissolution curves for sample 1 undispersed (◇) and dispersed in sugar at ratios 1:5 (△), 1:10 (○) and 1:20 (□). Particle size was 250 μm.

dispersing medium. By dividing the measured shear stress values by these background values, relative logarithmic values were calculated

$$\sigma_{\text{relative}} = \log(\sigma/\sigma_{\text{background}}) \tag{6}$$

where σ_{relative} is the corrected shear stress, σ the measured shear stress and $\sigma_{\text{background}}$ the shear stress measured for the solvent including totally dissolved dispersing media in its final concentration. The amount dissolved can then be calculated in the same way as for concentration values

$$m = (\sigma_{\text{relative}}/\sigma_{\text{relative},\infty})100\% \tag{7}$$

where $\sigma_{\text{relative},\infty}$ is the final relative shear stress value.

The calculated values for the amount dissolved can be fitted to the following equation

$$m = m_{\infty}\,(1 - \exp(-k(t - t'))) \tag{8}$$

where m_{∞} is the final amount dissolved, close to 100% depending on how good the fit is, k is a constant with dimension time^{-1} quantifying the dissolution rate, t is the time and t' is a time constant partly related to the time needed to hydrate the particle, but also includes variations in time needed to add the sample manually. Fig. 4 shows the resulting dissolution curves when these methods are applied to the measured values from Fig. 3. As shown, the dissolution rate is exactly the same when a standard curve is used compared to direct use of shear stress values. This implies that in similar systems, a standard curve is not necessary if dissolution rates are to be investigated.

The reproducibility of the method was examined by running three parallels for two different alginates, sample 2 and 4. The rate constants varied no more than 3–4% ($\pm 0.001\ \text{s}^{-1}$).

3.1.4. Dispersing effects

Compared to sugar dispersion, it is evident that alginate dissolves at a higher rate when dispersed in ethanol (Fig. 5), suggesting that this method distributes the alginate particles in the solvent more effectively. Additionally, the particle pores will be filled with another fluid, and this will reduce the affinity for water, initially giving a lower particle surface viscosity, and hence reduce the tendency for lump formation. Altogether, this has a positive effect on the dissolution rate.

To investigate the effect of different levels of dispersing agent, both non-dispersed alginate and alginate dispersed in sugar at different ratios were dissolved in water (Fig. 6). This alginate sample had particle size 250 μm. Clearly, dispersing the sample in sugar has a positive effect on hydrating the particles, but there is little effect of increasing the dispersing ratio to above 1:5. This independence of the dispersing ratio will probably be a function of the particle size; a finer alginate powder will need more dispersing agent. Attempts were made to dissolve a low molecular weight alginate, particle size below 45 μm, using sugar as

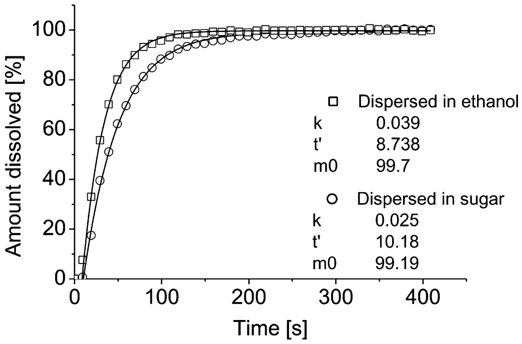

Fig. 5. Ethanol as dispersing medium compared to sugar for sample 2. Alginate/sugar ratio was 1:10, and alginate/ethanol ratio was 3:10 (w/v). Particle size was 250 μm.

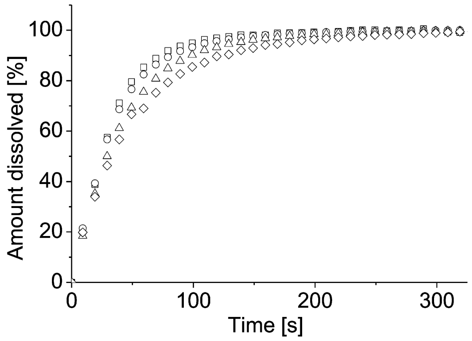

Fig. 7. Dissolution curves for sample 1 at different agitation speeds, 326.0 (◇), 435.5 (△), 543.5 (○) and 703.5 rpm (□). Dispersing ratio was 1:10.

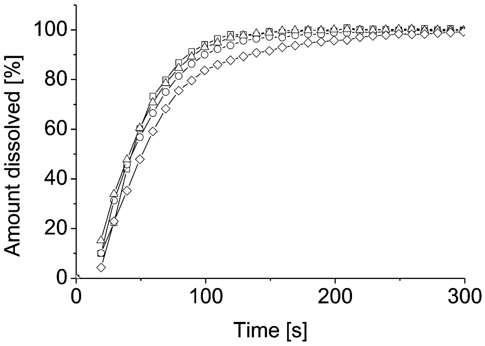

Fig. 8. Dissolution curves and dissolution rates for four alginates (samples 7–10) with 1% viscosity 1970 (◇), 768 (△), 414 (○) and 130 mPa s (□). Particle size was 190–250 μm and dispersing ratio 1:10.

dispersing agent, but lumps were hard to avoid even at dispersing ratios above 1:20.

Ideally, a good dispersion allows each particle to solubilize separately. If this is the case for ethanol and not for sugar dispersion is not known. It might be that sugar is not sufficient to disperse the finest particles and thus not totally preventing agglomeration.

3.1.5. Effect of agitation speed

The agitation speed affects the dissolution rate by altering the convective conditions in the solution. By lowering the agitation speed, the particles will dissolve at a lower rate as a result of reduced mass transport at the particle surface (Fig. 7). Attempts to dissolve dispersed alginate at rates lower than 326 rpm were made, but at this speed, sedimentation of both sugar and alginate particles became a problem. Still, Fig. 7 clearly shows the effect of reduced agitation speed in the range tested.

3.2. Effects of particle and solvent conditions

3.2.1. Effect of viscosity

The effect of viscosity on the dissolution rate was investigated for four alginates with the same range of particle size prepared by sieving (Fig. 8). The results indicate that the molecular weight, and therefore the viscosity, has little effect on the dissolution rate. The difference seems to be more profound at the end of the dissolution process where the largest viscosity differences are experienced, an observation in accordance with the fact that higher viscosity reduces the diffusion in the solvent.

Table 3
Rate constants for sample 1, dispersed 1:21 in sugar, dissolved in water containing glycerol. The final dry matter content was 0, 50 and 70%. Particle size was 75–125 μm

Dry matter content (%)	K (min^{-1})
0	2.46
50	0.91
70	0.089

3.2.2. Effect of particle size

Sample 3 was sieved into 6 particle size fractions ranging from 250 down to 38 μm, and the fraction finer than 38 μm was also collected. The dissolution kinetics for these fractions were determined, giving a reduction in the dissolution rate as the particle size increased (Fig. 9). These results support the theory that the dissolution process is surface dependent in addition to be diffusion limited. It is also interesting to see how fast alginate powder can dissolve if the conditions are optimal. For the 38 μm fraction, the rate constant is close to 0.5 s^{-1}, meaning that 90 percent of the alginate was dissolved in less than 10 s after addition. This is in sharp contrast to situations where non-dispersed, fine powders need dissolution times up to 20 min under heavy agitation due to the strong tendency to aggregate and form lumps at low particle sizes.

Sample 3 is an alginate with relatively low molecular weight, which generally dissolves fast because of low surface viscosity and hence reduced need for dispersion. This made it possible to dissolve fractions with particle size 38 μm and finer without lump formation, a difficult task for more viscous alginates which tend to form lumps at 75 μm and finer independent of dispersing ratio. For investigating the dissolution processes for such fine powders, ethanol has to be used as dispersion medium.

3.2.3. Dry matter content

Many alginate applications include dissolution of

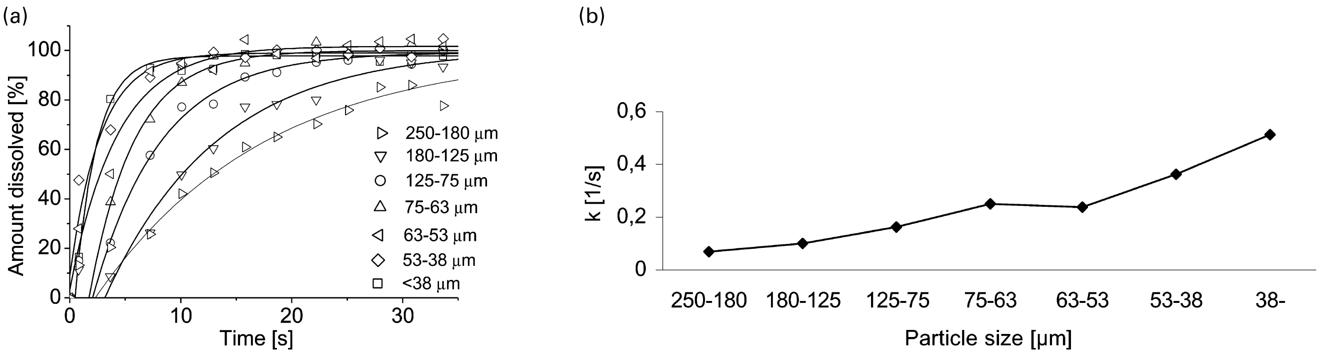

Fig. 9. (a) Dissolution curves and (b) rate constants for sample 3 as function of particle size. The alginate was dispersed 1:10 in sugar.

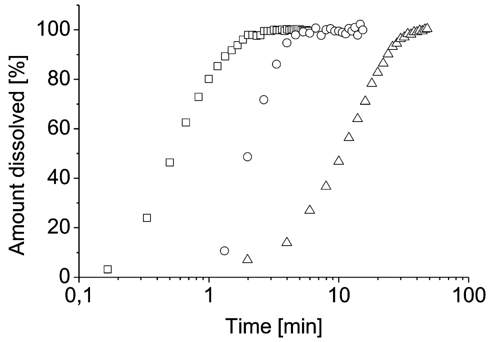

Fig. 10. Dissolution curves for sample 1 dissolved in 0 (□), 50 (○) and 70% (△) glycerol solutions.

alginate powders in systems containing high amounts of dry matter, for instance high sugar products in food applications. It is well known that the dissolution rate is reduced under such conditions, and like sugars, glycerol reduces the dissolution rate.

Alginate was dissolved in pure water, and water containing 50 and 70% glycerol (w/w) (Fig. 10). Table 3 shows the dissolution parameters for these experiments; note that the dimensions for time are in minutes, not seconds. The same alginate dissolved in pure water has a rate constant 2.46 min^{-1}, so the dissolution rate is almost reduced by a factor 30 when dissolving the same sample in water containing 70% glycerol.

One of the reasons for the reduced rate constant is that the water activity will be significantly reduced at such high glycerol levels. To minimize dissolution times in such situations it will be especially important to use alginates with fine particle size, effective mixing and good dispersion. Elevated temperature is also possible.

A lowering of the dielectric constant of the solvent by addition of glycerol will also increase the counter ion condensation according to the Manning theory (Manning, 1978) and thus reduce the rate of diffusion of alginate according to the Nernst–Hartley equation.

3.2.4. Dissolution rate in the presence of salts

Na-alginate and K-alginate were dissolved at different concentrations of NaCl and compared with respect to rate constant and time constant (Fig. 11). Both alginates dissolve at a slower rate with increased salt concentration in the solvent, and the degree of reduction is quite similar for both alginate salts. This must be caused by the reduced electrostatic interaction between the alginate polyanions and the counterion at increased ionic strength.

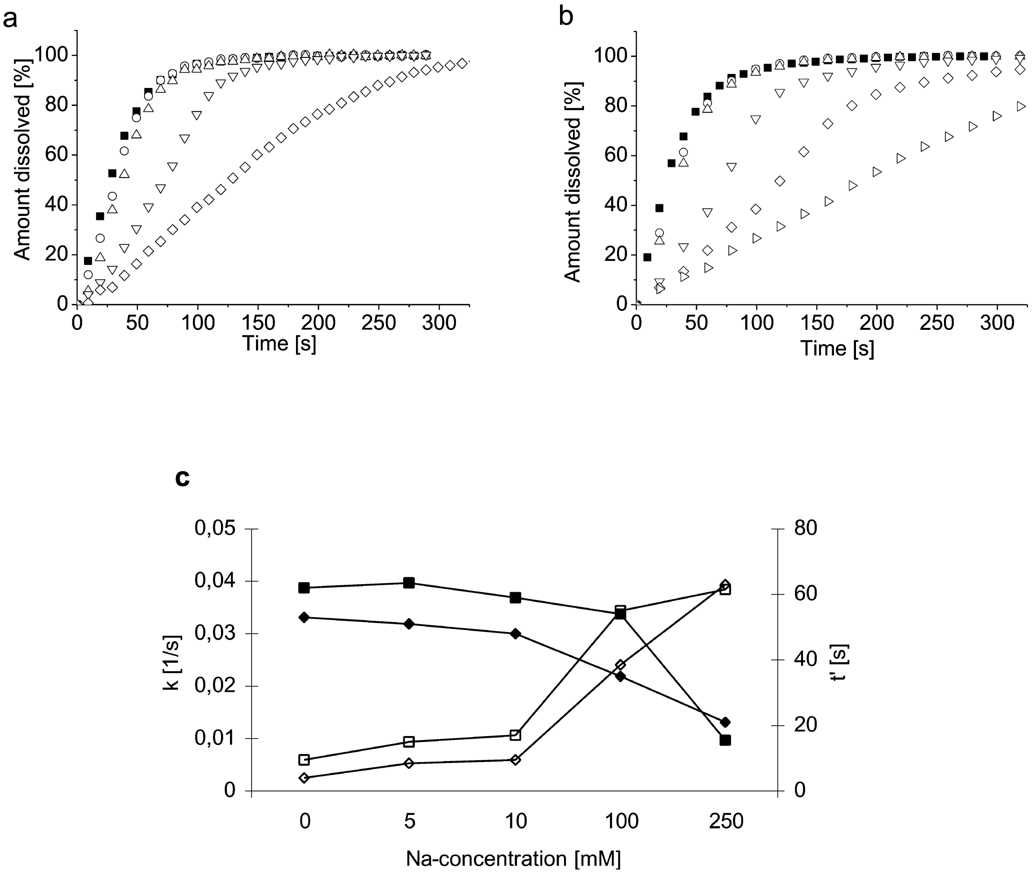

Fig. 11. (a) Dissolution curves for Na-alginate (sample 1) in solutions with different NaCl concentrations. (b) Dissolution curves for K-alginate (sample 9) in solutions with different NaCl concentrations. ■: 0, ○: 5, △: 10, ▽: 100, ◇: 250 and ▷ : 500 mM NaCl. (c) Rate constant, *k*, (closed symbols) and time constant, t', (open symbols) for Na-alginate (squares) and K-alginate (diamonds). Particle size was 125–180 μm.

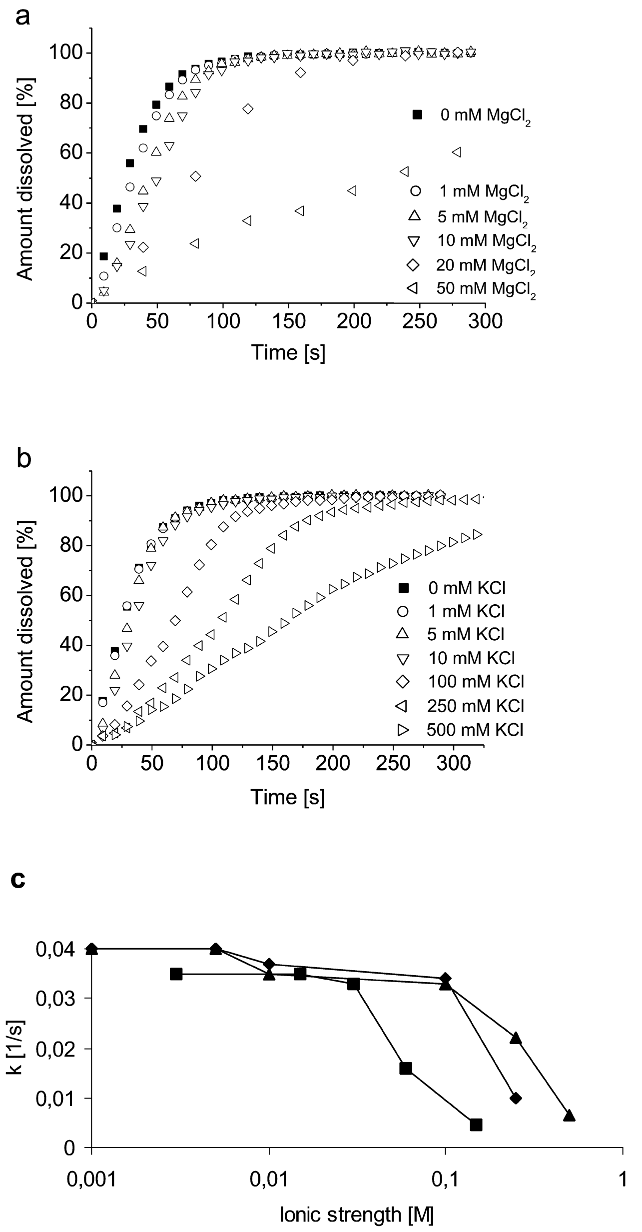

Fig. 12. Dissolution curves for Na-alginate, sample 1 in (a) $MgCl_2$ and (b) KCl. Particle size was 125–180 μm. (c) The rate constants for sample 1 at different ionic strengths of Mg^{2+} (■), Na^+ (◆) and K^+ (▲).

Sodium alginate dissolves faster than potassium alginate for salt concentrations up to 100 mM. This is to some extent surprising since the potassium ion is less strongly associated to the alginate molecule than the sodium ions (Draget, Steinsvåg, Onsøyen, & Smidsrød, 1998). However, other factors like e.g. different packing of the chain in the solid state, particle structure or differences in the solution of the free counterions may also contribute to the dissolution rate.

The reduced alginate solubility in highly concentrated KCl- and $MgCl_2$-solutions is well known (Haug & Smidsrød, 1968), and these salts also reduce the dissolution rate of sodium alginates (Fig. 12). The rate constants drop prominently when the levels of KCl exceed 0.1 M and the levels of $MgCl_2$ exceed 0.01 M.

When compared at the same and high values of ionic strength (Fig. 12(c)), the $MgCl_2$ gives a marked lower dissolution rate than the sodium and potassium salts, and this can easily be qualitatively related to differences in diffusion rate according to the Nernst–Hartley equation. When the sodium alginate molecules diffuse into an excess of magnesium ions a rapid ion exchange will occur decreasing the number of free counterions $|Z_{\mathrm{Alg}}^{\mathrm{eff}}|$ because of the divalent nature of the magnesium ions and the strongly enhanced counter ion condensation (Manning, 1978) of such ions compared to the monovalent sodium ion.

Dissolution of alginate in systems containing Ca^{2+} is different due to gel formation. Attempts to dissolve alginate particles in Ca^{2+}-solutions usually results in gel formation on the particle surface, and hence incomplete hydration and dissolution. The undissolved particles swell to many times their original size if the calcium concentration is low, or almost not swell at all if calcium concentration is high. Dissolution of alginate at different Ca-concentrations showed that, in a relative narrow range of Ca^{2+}-concentration, the final shear stress value exceeded the shear stress value for the same alginate in water, as shown in Fig. 13. These results are in accordance to earlier investigations on viscosity maxima in Ca-solutions (Smidsrød & Haug, 1965).

Incomplete dissolution (fish eyes) was observed already at Ca^{2+}-concentrations 1.5–2.0 mM.

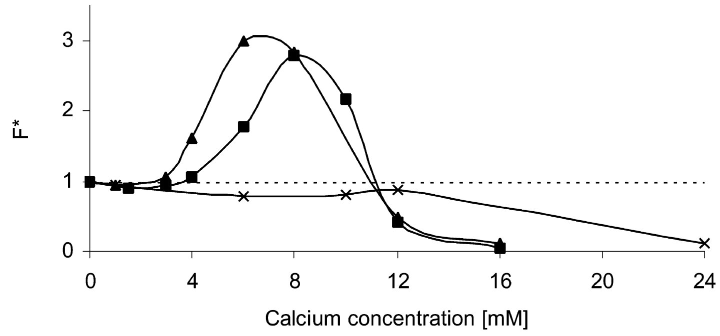

Fig. 13. The ratio F^* between the value of the shear stress in the calcium solution and the shear stress in pure water for three alginates with different M and G content, sample 2(■), 66% G residues, sample 11 (▲), 32% G residues and sample 10 (×), 0% G residues. Sample 2 and 11 had particle size 125–180 μm, and mannuronan particle size 75–125 μm. The alginate concentrations were 1.0% except for mannuronan (0.33%).

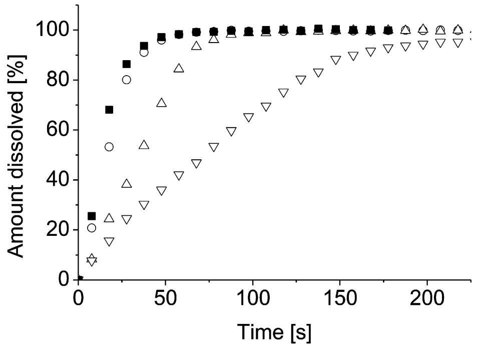

Fig. 14. Dissolution curves for mannuronan in calcium solutions. ■: 0, ○: 1, △: 6 and ▽: 12 mM $CaCl_2$.

The only alginate that showed solubility up to 12 mM $CaCl_2$ was mannuronan, Fig. 14. Mannuronan consist of only M-residues, and is a very stiff molecule compared to high-M alginates. Since mannuronan lacks gel-forming G-blocks it is not surprising that it is relatively soluble in Ca-solutions.

3.2.5. Temperature dependence

The rheometer allows measurements at temperatures ranging from 5 to above 100 °C, and alginate was dissolved in pure water at 10° intervals (Fig. 15). Fig. 16 gives the rate constants. By plotting $\ln k$ against $1/T$, done in Fig. 17, it was shown that the rate constant's temperature dependence followed Arrhenius' law;

$$k = A\,\mathrm{e}^{-E_a/RT} \tag{9}$$

or logarithmically;

$$\ln k = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right) \tag{10}$$

where k is the rate constant, A is the frequency factor, E_a the activation energy, R the universal gas constant and T the temperature in Kelvin.

A plot of $\ln k$ against $1/T$ will give the slope E_a/R. For sample 1, the activation energy was found to be 23 kJ/mol, which is close to the activation energy for self-diffusion of water 20 kJ/mol, (Mikhailov, Young, Lindhardt, & Mayo, 1999). This supports the assumption of diffusion controlled dissolution process.

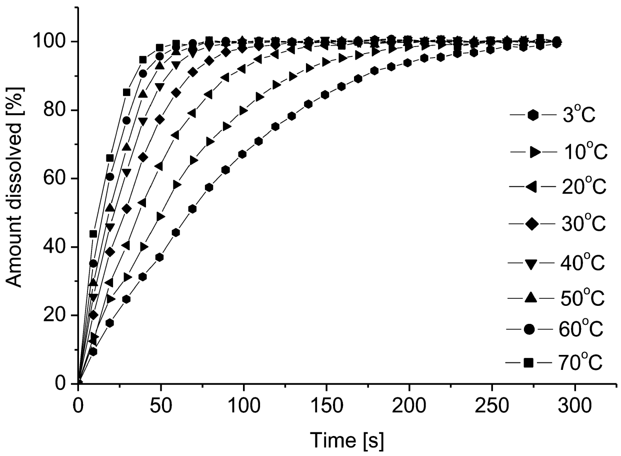

Fig. 15. Dissolution curves for sample 1 at different temperatures. Particle size was 180–250 μm.

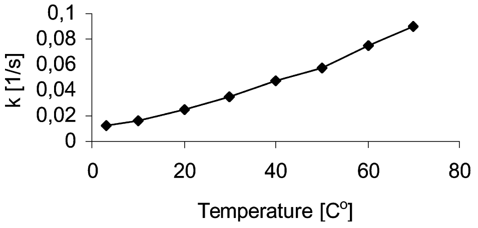

Fig. 16. Rate constant k for sample 1 obtained from the dissolution curves in Fig. 15.

3.2.6. The effect of a non-ionic polymer in the solvent

The impact of having a partly hydrophobic, non-ionic polymer in the solvent was investigated using polyethylene glycol, PEG (MW 30,000) (Fig. 18). Alginate was dissolved in PEG solutions, and above 10% PEG a profound reduction in the dissolution rate constant is observed. Unlike glycerol, PEG actually reduces the solubility of alginate. Another fact is that the limited water availability reduces the entropy gain for the alginate chains, which will have a more ordered conformation at high PEG-levels. A reduced dielectric constant of the solution may also contribute to the effects.

4. Conclusions

A method for determination of hydration and dissolution kinetics for well dispersed alginate powders was developed using a rheometer. By using the shear stress value as a parameter for viscosity and relating the values to the background contribution, it was possible to draw relative dissolution curves. To quantify the dissolution rate, these curves were fitted to an exponential function, and rate constants were obtained. The dissolution rate decreased with increasing salt concentration and increased particle size. Temperature dependence was found to follow Arrhenius' law, giving the activation energy 23 kJ/mol for the dissolution of an alginate in pure water. This is close to the activation energy for self-diffusion of water, indicating that the dissolution of alginate is a diffusion limited process. The dissolution rate is dramatically reduced in systems

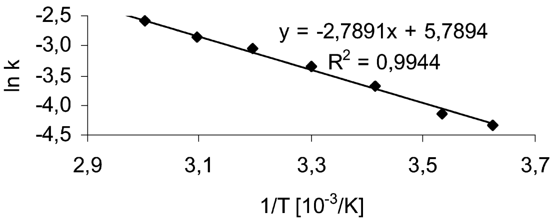

Fig. 17. Linear regression of a plot of $\ln k$ against $1/T$ for the rate constant calculated in Fig. 16 gives the rise −2789.1 K.

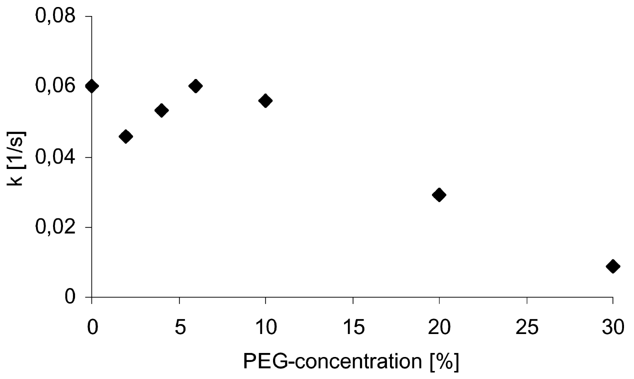

Fig. 18. Dissolution rate constants for dissolution of sample 1 in PEG-solutions.

containing high amounts of dry matter; the dissolution rate for an alginate sample was reduced by a factor 27 when dissolved in a 70% glycerol solution. A compound like PEG, that reduces alginate solubility, also reduces dissolution rates at concentrations lower than the critical solubility concentration. In general the data were found to be in good qualitative agreement with the diffusion theory of multicomponent polyelectrolyte systems.

The method showed good reproducibility, indicating that dispersing the powders is a crucial issue. The dispersing ratio did not affect the dissolution rate, as long as the powders were dispersed to a critical ratio.

Acknowledgments

Monica Bendiksen (FMC BioPolymer) is thanked for valuable support and discussions on rheological issues during this work.

References

Barthel, J., Krienke, H., & Kunz, W. (1998). *Physical chemistry of electrolyte solutions—Modern aspects*. Darmstadt: Steinkopff, p. 172.

Cantor, C. R., & Schimmel, P. R. (1980). *Biophysical chemistry*. New York: Freeman, Part II, Chapter 10.

Devotta, I., Ambeskar, V. D., Mandhare, A. B., & Mashelkar, R. A. (1994). The life time of a dissolving polymeric particle. *Chemical Engineering Science*, *49*, 645–654.

Draget, K. I., Steinsvåg, S., Onsøyen, E., & Smidsrød, O. (1998). Na- and K-alginate: Effect on Ca^{2+}-gelation. *Carbohydrate Polymers*, *35*, 1–6.

Foster, S., Schmidt, M., & Antonietti, A. (1990). Real-time X-ray scattering study during the thermal conversion of a precursor polymer to poly(phenylene vinylene). *Polymer*, *31*, 781–791.

Grasdalen, H. (1983). High-field ^{1}H-NMR spectroscopy of alginate: Sequential structure and linkage conformations. *Carbohydrate Research*, *118*, 255–260.

Haug, A., & Smidsrød, O. (1968). The solubility of polysaccharides in salt solutions. *Chemical Society Special Publication*, *23*, 273–282.

Hodgson, D. F., & Amis, E. J. (1993). In M. Hara (Ed.), *Polyelectrolytes: Science and technology* (pp. 127–191). New York: Marcel Dekker, Chapter 3.

Kravtchenko, T. P., Renoir, J., Parker, A., & Brigand, G. (1999). A novel method for determining the dissolution kinetics for hydrocolloid powders. *Food Hydrocolloids*, *13*, 219–225.

Lin, S. C., Lee, W. I., & Schurr, J. M. (1978). Brownian motion of highly charged poly(L-lysine). Effect of salt and polyion concentration. *Biopolymers*, *17*, 1041–1064.

Manning, G. R. (1978). The molecular theory of polyelectrolyte solutions with applications to the electrostatic properties of polynucleotides. *Quarterly Reviews of Biophysics*, *11*, 179.

Mikhailov, D., Young, H. C., Lindhardt, R. J., & Mayo, K. H. (1999). Heparin dodecasaccharide binding to platelet factor-4 and growth-related protein-α. *Journal of Biological Chemistry*, *274*(39), 25317–25329.

Moe, S. T., Draget, K. I., Skjåk-Bræk, G., & Smidsrød, O. (1995). Alginates. In A. Stephen (Ed.), *Food polysaccharides and their applications* (pp. 245–286). New York: Marcel Dekker.

Ranade, V. V., & Mashelkar, R. A. (1995). Convective diffusion from a dissolving polymeric particle. *American Institute of Chemical Engineering Journal*, *41*, 666–676.

Smidsrød, O., & Haug, A. (1965). The effect of divalent metals on the properties of alginate solutions. I. Calcium ions. *Acta Chemica Scandinavica*, *19*, 329–340.

Tanford, C. (1961). *Physical chemistry of macromolecules*. New York: Wiley, Chapter 21c.

Thu, B., Gåserød, O., Paus, D., Mikkelsen, A., Skjåk-Bræk, G., Toffanin, R., Vittur, F., & Rizzo, R. (2000). Inhomogeneous alginate gel spheres: An assessment of the polymer gradients by synchrotron radiation-induced X-ray emission, magnetic resonance microimaging, and mathematical modeling. *Biopolymers*, *53*, 60–71.

To, K. M., Mitchell, J. R., Hill, S. E., Bardon, L. A., & Matthews, P. (1994). Measurements of hydration of polysaccharides. *Food Hydrocolloids*, *8*, 243–249.

Treml, H., & Kohler, H.-H. (2000). Coupling of diffusion and reaction in the process of capillary formation in alginate gel. *Chemical Physics*, *252*, 199–208.