**FOOD
HYDROCOLLOIDS**

A novel method for determining the dissolution kinetics of hydrocolloid powders

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Abstract

Food hydrocolloids are sold as powders so they must be dissolved before use. In modern manufacturing practice, rapid dissolution can be an important specification. However, quantifying dissolution kinetics is a problem, because when lumps form the process becomes irreproducible, partly because lumps tend to stick to the stirrer. This paper presents a simple method for determining the dissolution kinetics of soluble polymer powders which solves these problems. The dissolution kinetics were followed using a modified rotational viscometer. The key modification is that when the powder is added, there is a vortex below the axis of the rotor, so that the powder cannot stick to it. The amount of hydrocolloid dissolved is followed via the torque on the viscometer. Measurements were performed under both dispersing and non-dispersing conditions. Under dispersing conditions each powder grain dissolves individually, and it is shown that the dissolution rate is proportional to the amount of powder surface. Under non-dispersing conditions, grains can stick together, forming lumps. The reproducibility of the method under both conditions is demonstrated using pectin. It was used to quantify the empirical observation that reducing the powder grain size increases the dissolution rate, but it also greatly increases lump formation. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Food hydrocolloids; Dissolution kinetics; Pectin

1. Introduction

Most food additives are sold in powdered form and must be dissolved in a liquid before use. Their solubility and dissolution kinetics are thus important factors in food processing, so evaluation of dissolution rates is important in the development, formulation and quality control of food hydrocolloids.

The dissolution kinetics of non-polymeric chemicals are usually studied using a batch method. The solid powder is immersed in the solvent under suitable agitation or stirring and the solute concentration is monitored as a function of time, usually by sampling and determining the solution concentration after removal of solid particles. This type of measurement is important in drug development (Abdou, 1989; Brittain, 1995; Grant & Brittain, 1995).

Polymer dissolution is much more complicated than that of low molecular weight solids (Brochard & de Gennes, 1983; Peppas, Wu, & von Meerwall, 1994; Tu & Ouano, 1977). The dissolution proceeds through a series of steps such as the transition from a glassy to a rubbery state, swelling of the rubbery polymer, disentanglement of the polymer chains from the surface of the swollen layer, and finally the movement of the free polymer chain into the bulk through the boundary layer. The dissolution process is the combined result of two phenomena namely the solvent penetration and the polymer dissolution. Unlike powders of non-polymeric molecules, penetration of the solvent into a polymer first induces swelling of the particle surface, forming a gel. Brochard and de Gennes (1983) discussed the effects of these phenomena on the dissolution of concentrated polymer droplets in unstirred solvent. More recently, Devotta, Ambeskar, Mandhare, and Mashelkar (1994) and Ranade and Mashelkar (1995) have developed, and verified experimentally, a sophisticated model for the dissolution kinetics of an isolated polymer particle in a stirred solution.

The gel layer which forms immediately after polymer/solvent contact is highly viscous and extremely sticky, so its presence can lead to problems of lump formation when powder beds are tipped into solvent. Lump formation has a great influence on the dissolution kinetics and also causes experimental difficulties for measuring dissolution rates.

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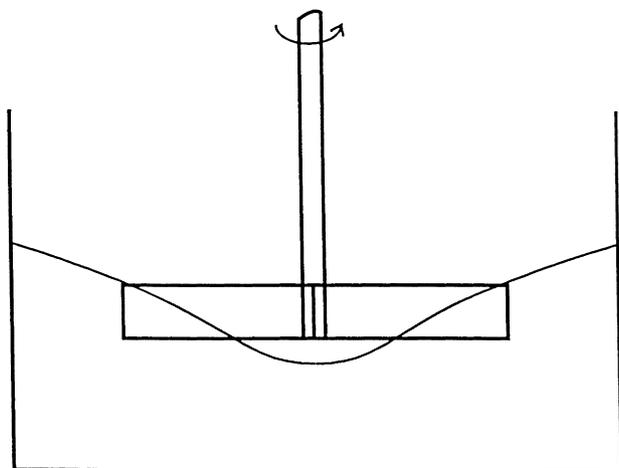[2] Present address: Firmenich S.A, 1 route des jeunes, CH-1211 Geneva 8, Switzerland.

Fig. 1. Stirrer position in order to maintain the bottom of the vortex in the dispersion medium below the bottom of the stirrer axis.

Despite its technological importance, we have not found any previous studies of the formation of lumps during polymer dissolution, either experimental or theoretical.

This article presents a novel procedure allowing reproducible determination of the dissolution kinetics of beds of hydrocolloid powders. The results can be interpreted to obtain the sample's dissolution rate, but also to quantify its ability to be dispersed without forming lumps. Pectin is used to demonstrate the method.

2. Materials and methods

The pectin was a high methoxyl lemon pectin (degree of methoxylation: 67%) produced by SKW Biosystems (France). The powder was obtained, as usual, by precipitation of the soluble pectin extract in isopropanol, followed by drying and grinding. It was divided into size fractions using a vibrating sieve (Retsch, RFA).

The exact geometry of the apparatus for measuring the dissolution kinetics is the key to our method. It was the result of a large amount of empirical testing. The factors governing the design are discussed in Section 3.1. Dissolution was carried out in a 500 ml crystallising dish (height, 65 mm and diameter, 110 mm), filled with 300 ml of deionised water. The solvent was stirred using a Haake VT550 viscometer fitted with a home-made four-blade impeller, revolving at 240 rpm. Each blade was a vertical flat plate 32 mm long and 14 mm deep. The viscometer was also used to record changes in torque caused by dissolution. Powders (1 g of pectin or 1 g of pectin intimately mixed with 18 g of sucrose) were tipped reproducibly into the dissolution vessel from a PTFE-coated beaker attached to an electric motor which rotated rapidly through 180°. The beaker was placed 10 cm above the unstirred water surface. Both the motor for powder addition and the viscometer were interfaced to a microcomputer.

The particle size distribution of the powder was measured by small angle light scattering using a Malvern MasterSizer fitted with the 300 mm focal length lens. The Malvern software converted the raw data into a particle size distribution using the Fraunhofer approximation for their optical properties (the grains are assumed to be black circles), which is valid for particles with diameters above a few microns. The dispersing medium was 96% isopropanol in which pectin is insoluble.

The density of the dry powder was determined by measuring the volume occupied by a known mass of pectin powder. The powder was weighed in a volumetric flask which was then filled with 96% isopropanol. The mass of the added isopropanol was measured to calculate its volume and the volume of the powder particles was calculated from the difference. The density of the powder was found to be 1.48 g cm^{-3}.

3. Results and discussion

3.1. Apparatus design

Stirring is easy to perform by rotating a stirrer in the dissolution medium. The problem with polymer powders is that they tend to stick to surfaces, including the stirrer, causing irreproducible results. Careful design of the measuring system was necessary in order to obtain reproducible measurements of the dissolution kinetics.

Rotation of a stirrer immersed in a solvent causes a vortex to form. In the usual geometries this effect drives the powder particles into contact with the stirrer axis. Fig. 1 shows that in our set-up this phenomenon is prevented by stirring fast enough to form a significant vortex and setting the stirrer high enough to keep the bottom of the vortex below the bottom of the stirrer axis. When the powder is added, only the tips of the four stirrer blades are wetted. This novel geometry prevents the powder from sticking to the stirrer. As the dissolution proceeds, the viscosity increases and the depth of the vortex decreases, but at this point, adhesion of the dissolving individual particles and/or lumps is no longer a problem. This is an interesting observation in itself, as it shows that during wetting, a hydrocolloid powder is only sticky for a short time after its first contact with water.

Owing to their large hydrodynamic volume, dissolved polymer molecules generate a high viscosity. This property has been used to follow the concentration of the dissolved polymer during dissolution experiments. The torque on the axis of the stirrer is proportional to the viscosity of the solution and hence to the dissolved polymer concentration.

3.2. Measurement protocols

Two measurement conditions were used namely dispersing and non-dispersing. Non-dispersing conditions were obtained by rapidly tipping 1 g of pectin into the dissolution vessel. This protocol allows lumps to form. Dispersing
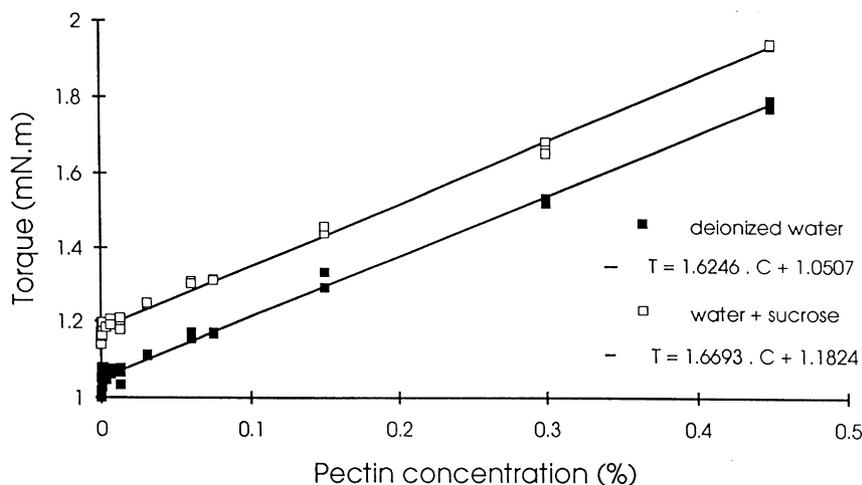
Fig. 2. Torque versus dissolved pectin mass in deionised water and in 6% aqueous sucrose solution.

conditions were obtained by intimately mixing 1 g of pectin with an excess of ground sucrose with roughly the same grain size (sieved to below 100 μm). This is a well known method in food technology to ensure good hydrocolloid dispersion. It was found that 18 g of sucrose was sufficient to prevent lump formation in even the most lump-prone samples.

The presence of the dissolved dispersing agent, sucrose, at the concentration used here (18 g in 300 ml) increases the viscosity of the dispersion medium slightly. Fig. 2 shows the relation between the pectin concentration and the measured torque for the sample studied in the presence and absence of sucrose.

The undissolved powder grains cause a negligible viscosity increase, as the following argument shows. A dilute suspension of spherical particles behaves as a Newtonian liquid with a relative viscosity given by: $\eta_{rel} = (1 + 2.5\varphi)$, where φ is the volume fraction occupied by the powder particles. Thus a powder at the concentration used here of 1 g in 300 ml, equivalent to $\varphi \approx 0.003$, makes a

negligible contribution to the measured torque. However, the viscosity generated by the solid sucrose particles cannot be neglected. Fig. 3 shows that their volume generates a steep viscosity increase when they are brought into contact with the solvent. However, this effect disappears very quickly as the sucrose dissolves.

The measured torque can be converted into concentration of dissolved pectin by applying the calibration curves shown in Fig. 2. However, these data were obtained by adding pectin to a 6% sucrose solution, whereas in dissolution experiments sucrose powder was added at the same time as the pectin. Sucrose requires some time to dissolve totally so that at time zero the measured torque is that of pure water. Fig. 3 shows the dissolution curve of sucrose in a 1% solution of the pectin tested. The sucrose dissolves completely in less than 20 s, so the calibration curve can be safely applied to torque values measured 30 s after powder addition. However, under dispersing conditions, the amount of dissolved polymer is unknown for the first 30 s after powder addition.
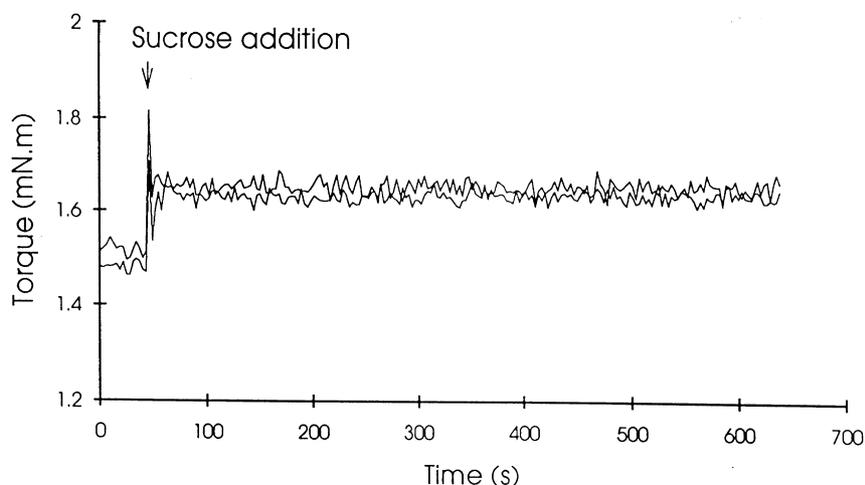

Fig. 3. The dissolution kinetics of sucrose in a 3.3 g l^{-1} pectin solution.

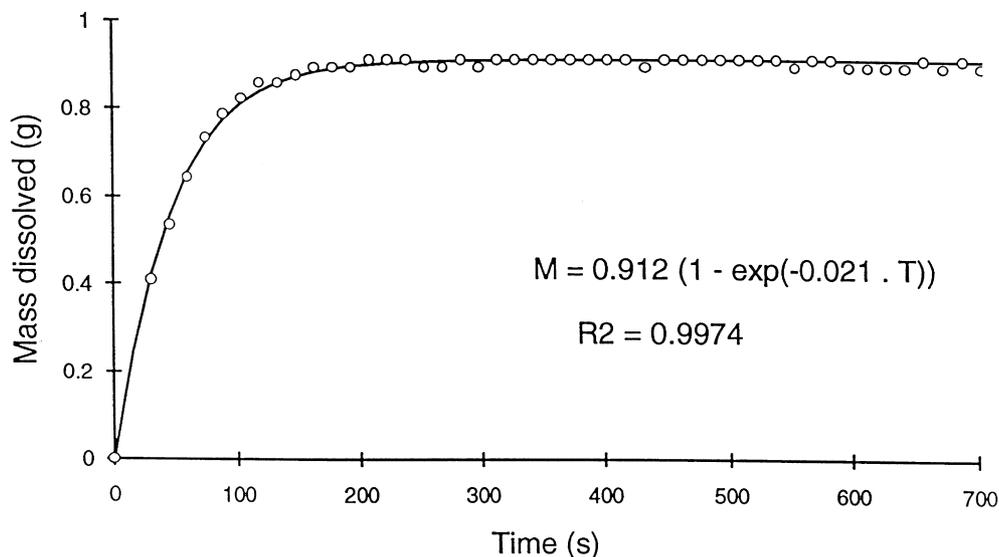$$M = 0.912 \, (1 - \exp(-0.021 \cdot T))$$

$$R2 = 0.9974$$

Fig. 4. The dissolution kinetics of pectin under dispersing conditions.

3.3. Dissolution under dispersing conditions

Fig. 4 shows a typical dissolution curve of a pectin powder under dispersing conditions. As To, Mitchell, Hill, Bardon, and Matthews (1994) found previously, the curve can be fitted empirically to an equation of the form:

$$m = m_\infty(1 - \exp(-kt)), \tag{1}$$

where m is the mass of polymer dissolved at time t and m_∞ is the final polymer mass dissolved. k quantifies the rate of dissolution of the pectin. Whilst Eq. (1) has the form of a first-order kinetics, this is only a coincidence, as in first-order kinetics all of the reactant is available for reaction at time zero, whereas during dissolution only the polymer at the surface can ''react''. Another objection to a physical interpretation of this equation is that its use implicitly assumes that the dissolution time is infinite, which is untrue.

Table 1 shows the results obtained from six independent measurements of the unsieved pectin sample. The dissolution rate constant k was found to vary from 0.021 to 0.025 s^{-1} with a variance of 2%. The fit to each dissolution curve always gave a correlation coefficient, R^2, higher than 0.990. Thus, k is a reproducible descriptor of the dissolution

Table 1

Results of six independent measurements of the particle dissolution rate of 1 g pectin powder under dispersing conditions: k and m_∞ are the parameters from Eq. (1)

Trial number	k (s^{-1})	m_∞ (g)	R^2
1	0.021	0.97	0.997
2	0.021	0.91	0.997
3	0.021	0.85	0.993
4	0.024	0.91	0.994
5	0.025	0.91	0.996
6	0.023	0.97	0.998

process for this powder sample. We call it the powder dissolution rate.

3.4. Dissolution under non-dispersing conditions

Fig. 5 shows the dissolution curve obtained with pectin in the absence of sugar. The measured torques were converted to concentrations using the corresponding calibration curve in Fig. 2. Note that measurements stopped after 30 min, when some lumps remained undissolved. The experimental data do not follow a single exponential, as under dispersing conditions, but were found to fit quite well a sum of two exponentials:

$$m = A(1 - \exp(-k_a t)) + B(1 - \exp(-k_b t)), \tag{2}$$

where $k_a > k_b$ and $A + B = 1$ g. Thus under non-dispersing conditions, there appear to be two independent processes, with the same kinetic equation, but different rates. The obvious interpretation is that the fast process is dissolution from well dispersed grains and the slow process is the dissolution of lumps. In this interpretation, A corresponds to the mass of polymer initially in the form of dispersed grains and B to that incorporated into lumps. The sum $A + B$ is equal to the final polymer mass dissolved. Lastly, k_a is the dissolution rate constant for dispersed grains and k_b that for lumps.

In this interpretation, A is the mass fraction of powder that disperses without forming lumps. We call $100A$ the index of dispersibility (ID). Table 2 shows the results of fitting Eq. (2) to data from six independent experiments. The ID was found to vary from 31% to 37% with a variance of less than 5%. We conclude that the ID is a reproducible descriptor of this powder's tendency to form lumps, or, in other words, its dispersibility.

It is interesting to note that the value of k_a, determined under non-dispersing conditions, is close to the value of k determined under dispersing conditions. This is evidence
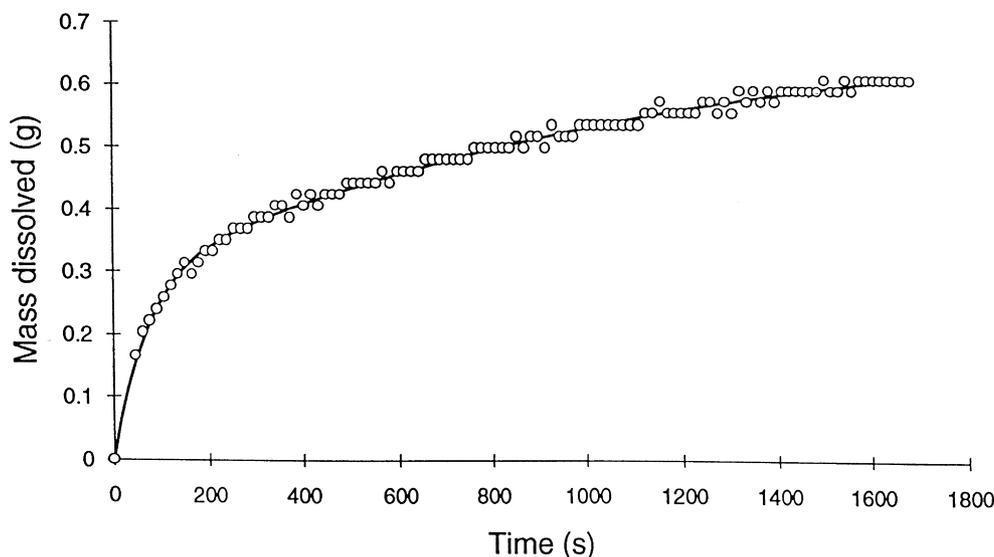
Fig. 5. The dissolution kinetics of pectin under non-dispersing conditions.

that the fast process modelled by Eq. (2) is in fact the dissolution of individual grains. In principle, a single experiment in the absence of dispersing agent would be sufficient to determine both k and the ID. However, Table 2 shows that the determination of k_a under non-dispersing conditions is less reproducible than that of k under dispersing conditions.

3.5. A physically realistic model for dissolution

Fig. 4 shows that under dispersing conditions the dissolution rate decreases regularly with time, up to a plateau where dissolution is complete. The simplest model for dissolution, well known in chemical engineering, assumes that the surface flux is constant. The surface flux, J, is defined as the volume of dry polymer dissolved per unit surface per unit time. With constant flux, it can be easily demonstrated that the mass dissolved from a sphere with initial radius R_0 increases as:

$$m = \tfrac{4}{3}\pi\rho[R_0^3 - (R_0 - Jt)^3] \qquad \text{for } t \le R_0/J, \tag{3a}$$

where ρ is the density of dry polymer. Note that this relation no longer applies when the volume reaches zero (i.e. once the particle is dissolved), at the dissolution time given by $R_0/$

J. At longer times m obviously remains constant, i.e.:

$$m = \tfrac{4}{3}\pi\rho R_0^3 \qquad \text{for } t > R_0/J. \tag{3b}$$

This model was used to calculate the form of the dissolution kinetics shown in Fig. 4 by numerically integrating the contribution from each size of grain. Fig. 6 shows the measured particle size distribution. It was assumed that the grains differed only in size (i.e. they had equal ρ and J). Once the shape of the curve was calculated, the data in Fig. 4 were fitted using the known density and adjusting the surface flux, J. Fig. 7 shows that the model gave a reasonable fit with a surface flux of 0.16 μm s^{-1}. The slight discrepancy between data and fit may be because of an error in the calculation of the particle size distribution. The conversion of light scattering data into a particle size distribution is not an exact science because many particle size distributions can give rise to exactly the same light scattering data. We have some evidence for such an error: though all the grains could pass through a 250 μm pore size sieve, the MasterSizer indicated the presence of larger grains. Another possible source of error is the assumption made by both the MasterSizer algorithm and the dissolution model that the particles are spherical, which they are not, so their dissolution kinetics will not follow Eqs. (3a) and (3b).

Nevertheless, the quality of the fit shown in Fig. 7 suggests that the assumptions of the model are valid, that is the surface flux is the same for all powder particles and constant throughout the dissolution process. We expect the surface flux to depend on the sample's physico-chemical characteristics (molecular weight, particle shape or density etc.) and also on the dissolution conditions (temperature, strength of mixing, presence of salts or sugar, etc.).

3.6. The effect of particle size

Particle size is an important characteristic of hydrocolloid

Table 2
Parameters obtained by fitting Eq. (2) to six independent measurements under non-dispersing conditions

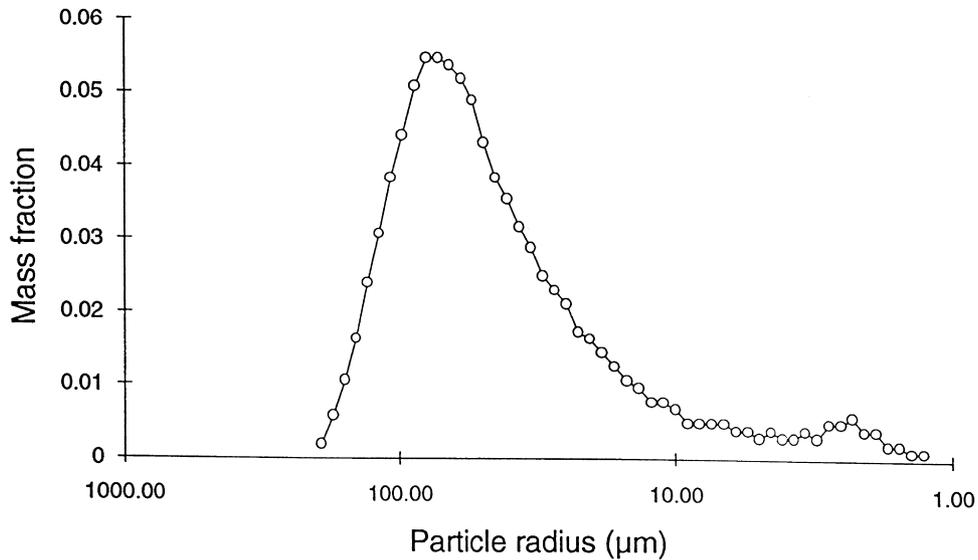| Trial no.	A (g)	k_a (s^{-1})	B (g)	k_b (s^{-1})	ID (%)
1	0.37	0.019	0.63	0.00035	37
2	0.34	0.012	0.66	0.00033	34
3	0.35	0.013	0.65	0.00050	35
4	0.32	0.013	0.68	0.00030	32
5	0.32	0.017	0.68	0.00034	32
6	0.31	0.019	0.69	0.00036	31

Fig. 6. The particle size distribution of the unsieved pectin sample determined by small angle light scattering.

powders. Empirically it is known that grinding more finely leads to a faster dissolution, but also to problems of lump formation, if taken too far. However, these observations have never been demonstrated quantitatively. To test them the pectin sample was fractionated using a series of sieves with 45, 63, 80, 100 and 125 μm pores. Each fraction was characterised by small angle light scattering and its dissolution determined under dispersing and non-dispersing conditions. Fig. 8 shows the influence of the volume average particle size on the dissolution parameters of the pectin sample. The index of dispersibility clearly increases with increasing particle size whereas, except for particles smaller than 45 μm, particle dissolution rate decreases. The effect of

particle size on particle dissolution rate is not surprising as smaller particles have a much larger surface in contact with the solvent. These results show that the empirical knowledge on the effects of reducing grain size on dissolution kinetics are correct.

Generalising further, we hypothesise that, as lump formation is almost certainly due to the rapid formation of a sticky layer at the surface of powder particles, any factor which increases the dissolution rate also decreases the dispersibility. Temperature is an example of such a factor: for best dispersion, it is better to mix the powder with cold water, rather than hot, in which dissolution is faster (unpublished data).
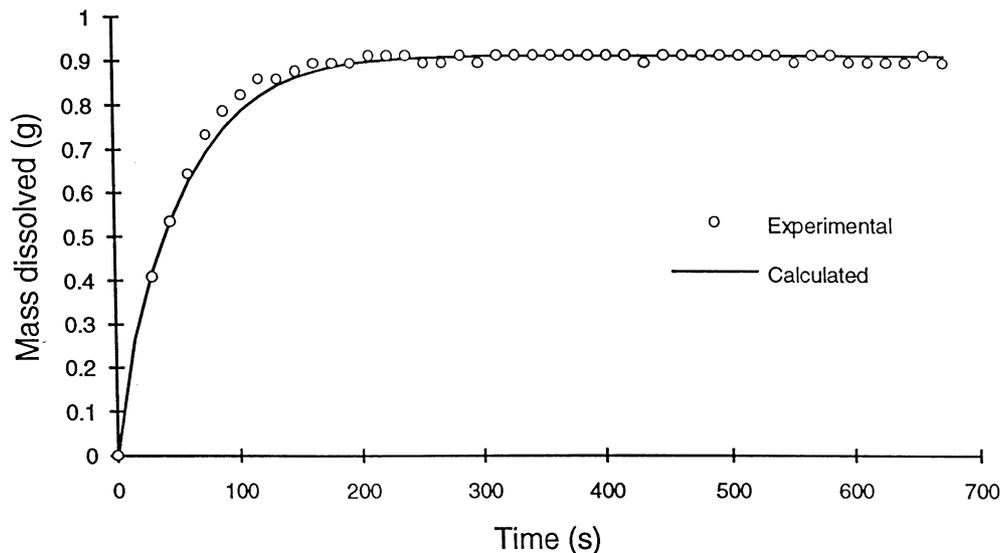

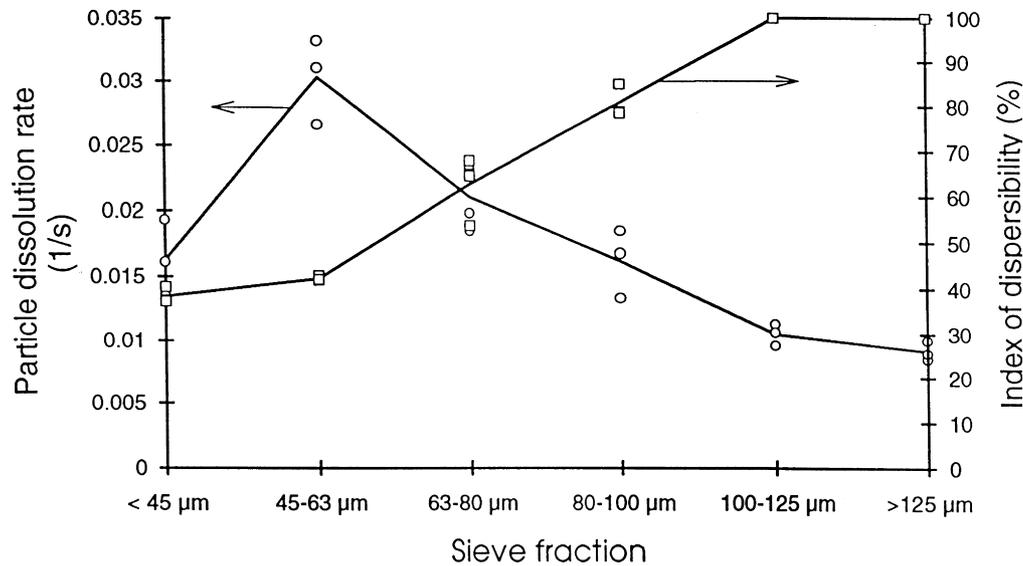Fig. 7. Fit of Eqs. (3a) and (3b) to the experimental data in Fig. 4.

Fig. 8. Influence of the grain size on the powder dissolution rate and the index of dispersibility.

4. Conclusions

The technique described here resolves two difficult experimental problems in measuring hydrocolloid dissolution kinetics: (a) lump formation is random, so it is hard to obtain reproducible results; (b) in the usual geometries, lumps stick to the stirrer, which changes their dissolution kinetics. By providing a solution to these problems, our set-up allows accurate quantification of important characteristics of hydrocolloids, which have only been estimated qualitatively up to now.

We have found this technique very useful for the study of the effects of various physico-chemical parameters of pectin powders, as well as the effect of the dissolution conditions (temperature, water hardness, etc.). It has also been used successfully to study the dissolution kinetics of other hydrocolloids, such as carrageenan, xanthan and guar.

Finally, it is important to point out that the exact correlation between results determined by this technique and those found in practice will vary depending on the strength of mixing used. To demonstrate this point, consider two extreme cases: on the one hand, sufficiently strong mixing and slow enough powder addition will prevent lump formation for all samples. On the other hand, gently placing a bed of powder on still water will almost always result in the formation of one large lump. The method described here allows the dispersibility of powders to be determined reproducibly at an arbitrary point between these two extremes. Hence the correlation between the results it provides and those found in any particular industrial set-up need to be discovered on a case by case basis.

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