**Kinetics of Food Biopolymer Film Dehydration: Experimental Studies and Mathematical Modelling**

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**ABSTRACT**

The dehydration process in thin biopolymer based films, involving the two main macromolecules in food systems, i.e. proteins and polysaccharides, has been investigated. Experimental measurements of the weight loss of polymer films were carried out in an enclosed Perspex chamber under controlled conditions of temperature, relative humidity and air flow. We find that all the experimental moisture ratio data for films of pure biopolymers, as well as their mixtures, can be superimposed on a single scaled dehydration curve. Performing theoretical calculations, it has been shown that this curve cannot be described by a moisture diffusion dominated drying process, irrespective of whether the film shrinkage is included or ignored. We also derived an analytical expression for the evaporation controlled drying. When the film shrinkage is fully accounted in the calculations, very good agreement between the experiments and theoretically derived curve is obtained. However, the theoretical results can be improved even further by considering a model that includes both diffusion and evaporation processes, with diffusion being fast but nonetheless finite, so as to only play a minor secondary role in dehydration of such films.

 Theoretical models have also been extended to describe systems where the film shrinkage can also arise from changes in the partial molar volumes, and not just loss of moisture. Using a variable “effective” partial molar volume for water, the result provides a possible way of modelling the entire drying process over different stages of dehydration, where the solid phase adopts significantly contrasting structure.

# 1. INTRODUCTION

Thin biopolymer films have many important applications in industry, particularly as adhesives1, paints2, in the food industry as edible coatings3, and the pharmaceutical industry as drug delivery systems.3, 4 The requirement and criteria are often very different for different dehydration applications. It is therefore important to understand the mechanisms involved in the drying process of these biopolymer films. For instance, if a film dries too rapidly, defects such as cracks and bubbles can occur which weaken the films and reduce their performance. On the other hand, if a film dries too slowly, dripping may occur for coating and labelling applications. Temperature, relative humidity and air flow velocity are important external parameters in controlling drying rate. However the diffusion of moisture within the internal film structure is also a major factor in how the film dries. Drying, in some cases, can be split into an initial constant rate period where free moisture from the surface is removed, followed by two falling rate periods whereby diffusion is the main transfer mechanism. However, this only applies to systems which start with a layer of saturated moisture on their surface and the initial moisture loss can be compensated fully by the fast moisture diffusion. Water can be present in different molecular environments depending on its interactions with the surrounding molecules. Initially, most of the water in a polymer network is in free water status (*a*w = 1) like those in a bulk phase water, surrounded by other water molecules, and can diffuse through the system without significant restriction. This so-called free water is lost during the constant rate and the first falling rate period. Once all the free water has evaporated, the rate of dehydration slows and the second falling rate period becomes apparent. Loosely bound water requires extra energy for either breaking up bonding or internal evaporation. At this stage, diffusion of water could be either in liquid or in vapour or in both. Practically, it is very difficult to differentiate the different mechanisms involved in moisture diffusion. Therefore, an effective, moisture dependant diffusion coefficient is used in the analysis of rate of dehydration. In most dehydration applications, bound water remains untouched in the dried film. Often, and particularly in foods, an initial constant rate period is not observed.5

During dehydration, changes in the structure of the polymer film may occur. The most prevalent of these changes is film shrinkage, which is directly related to moisture loss due to drying.6 As the film dries and moisture is lost, a pressure imbalance between the inside and outside of the film develops. This pressure imbalance results in the build up of mechanical stress within the film, which leads to possible shrinkage, collapse or cracking of the film in order to release the stress. The increase of stress and its subsequent decrease due to structural relaxation within a drying film has been experimentally measured by the authors.7 The dynamics of stress evolution within the film depends significantly on the internal structure of the film. The cracking of the film is most prevalent in drying of colloidal particulate dispersions, or solutions of film forming polymers below their glass transition temperature, where the structural relaxation times are long.8, 9 The porous structure allows moisture to migrate to the surface through these channels without film shrinkage or loss of volume during the drying process. Various models of transport, dealing in particular with the presence of porous structures in foods and similarly related biological systems, have been reviewed by Datta.10-12

Assumptions made in mathematical models to simulate such drying processes must reflect these diverse behaviours in order to provide an accurate and reliable representation of the drying process. During the drying of the biopolymer films used, initially, as moisture is lost from within the film, the film shrinks due to the lack of a stress supporting structure. There comes a point however, at which although moisture continues to be lost there is no further shrinkage and the solid fraction forms a porous structure with a yield stress that can support the stresses developed in the film. No further volume changes occur at this point. In order to be able to model the entire dehydration process encompassing both these different behaviours, it is important to consider the general case where effective molar volumes, if not the true values, of both the solid and the water phases alter during the process. This will be discussed in further detail in the theoretical considerations section.

There are many different methods reported to monitor and investigate aspects of drying. NMR diffusion measurements have been used to investigate microstructure changes in detergents during drying.13 This is a non-invasive technique which provided an insight into the behaviour of individual droplets within detergents. Schmidt-Hansberg *et al*14 used reflectometry to monitor the drying kinetics of polymer films. A laser beam was shone on the sample and the reflected beam was detected using a silicon photodiode, throughout the drying process, to collect data on the film thickness which was used to create moisture loss vs time curves. The intensity of fluorescence given off by polymers as they dry has also been monitored15, 16 where, as more water is released from a polymer, an increase in intensity of the pyranine based fluorescence is seen. Results obtained using this method are supported by gravimetric and volumetric data, and type II diffusion models, where Fick’s laws cannot describe the entire process, fit the data well.

The simplest method for monitoring drying kinetics is the gravimetric method. This is a macroscopic method that is the most prevalent of the techniques that are reported in the literature.6, 17-19 It is easily applicable to all shapes and sizes for a wide range of materials. It is a straightforward procedure where the sample is dried under controlled temperature and relative humidity, and the sample is weighed over set time intervals. The method is popular because the weight change with time is easy to measure, and if carried out *in situ*, does not cause any disturbance to the sample’s drying environment which could potentially lead to inaccuracies in the drying data. The method has also been used in the study of rehydration and ingress of water into polymer coatings, although this is a somewhat different problem to that of dehydration considered here.20

In most cases when thin films are dried, the controlling factor is diffusion of the moisture within the film.21, 22 The rate of evaporation when moisture reaches the surface is assumed rapid enough to be almost instantaneous and therefore does not influence the drying rate of the film. This is reflected in the simplest mathematical models by taking the moisture content at the surface of the film as always being at equilibrium with the moisture in the air above. Furthermore, such models are mostly based on Fick’s second law of diffusion with either a constant diffusion coefficient6, 17, 18, 23, 24, or in some a variable diffusion coefficient that changes with moisture ratio. More sophisticated models attempt to take shrinkage of the drying material into account, by using moving boundary conditions.19, 25 In most cases these simple mathematical models have been found to give a reasonable fit to experimental data, and in the literature many use these as a satisfactory approximation. However, as our work demonstrates a more complex model may be required to give a more reliable representation of the drying process.22

In this work the process of mass transfer during dehydration of several thin biopolymer films, under controlled temperature and relative humidity conditions, is studied. Experimental results will be compared with several mathematical models based on Fick’s second law of diffusion and incorporating the following different scenarios: i) the dehydration involves both constant and variable diffusion coefficients, as well as film shrinkage; ii) the diffusion is instantaneous and the evaporation rate is the controlling factor; and iii) both diffusion and evaporation have a role in controlling the drying rate. These models are discussed in detail in the theoretical considerations section that follows. The ultimate aim of this work is to establish a mathematical model which adequately describes the dehydration behaviour of thin biopolymer films.

# 2. EXPERIMENTAL METHOD

The samples investigated in the dehydration experiments were 18 wt% sodium caseinate (purchased from Acros organics) solution, 7 wt% purity starch solution (provided by Henkel), and a mixture of 9 wt% sodium caseinate and 4.5 wt% starch solution. The solutions were prepared by dissolving the powder in distilled water at 90 °C under magnetic stirring for 1.5 h. Sodium azide (0.02 wt%) was added as a preservative, and 10 drops of an anti-foaming agent were added to avoid the formation of bubbles.. All samples were stored at operating temperature and used within three days of preparation.

The dehydration experiments were carried out in a purpose built, wood framed Perspex chamber, with dimensions of 710 mm × 445 mm × 705 mm (length × width × height), designed and made in house. The chamber has an accurate temperature control that allows the chamber to be set at any temperature between room temperature and 50 °C. The relative humidity was controlled reliably by continuous supply of dry air and wet air, bubbled through pure water, into the chamber at a rate of 10L/min. The dry air was obtained by passing controlled air through a drying column (Beko drypoint). The ratio of wet to dry air can be controlled to achieve the desired relative humidity within the chamber. The chamber also has a fan to create a gentle air flow so that air homogeneity can be maintained throughout the entire system. The relative humidity conditions investigated include 20%, 30%, 40% and 50%, with the temperatures set to 30 °C, 40 °C and 50 °C. The chamber houses a beam coating system which consists of a moveable platform with a stainless steel beam (80 mm x 12.6 mm x 0.4 mm) attached. On the left hand side wall of the chamber is a coating gate of 0.4 mm. A small volume of thermally equilibrated sample was first deposited on the beam. The beam is then pulled though the coating gate at a constant speed using a stepper motor to ensure an even coating of film, with a thickness of 0.4 mm and width of 10.6 mm, across the full length of the beam. A diagram of the setup and the details of the procedure can also be found in a previous study where the development of stress within drying films was studied.7 The coated beam is then placed on a balance inside the chamber and the weight loss is monitored *in situ* at set time intervals for 4 hours.

**3. THEORETICAL CONSIDERATIONS**

In this section the drying process for a film, as applied to the biopolymer solutions discussed above, is considered from a theoretical point of view. Within the body of the film, the process of moisture transfer involves diffusion of water. On the upper surface of the film, i.e. the surface exposed to the surrounding air, the loss of water is due to evaporation. It is assumed that there is no loss of moisture through the substrate underneath the film and moisture loss through the side surfaces is also negligible. We shall first highlight some of the issues and complications that can arise in association with each of these two processes, before presenting our mathematical analysis of the drying model. In the simplest case, one can assume that the volume of the film remains constant throughout the drying process. This occurs if the solid fraction in the polymer film has formed a porous layer through which the water can migrate to the surface. Obviously, the yield stress of the porous structure formed in such a case must be sufficient to withstand any capillary stresses induced during the loss of moisture. Under such circumstances the much smaller diffusion of solid fraction can be ignored. Furthermore, since the loss of water from any region in the film is not accompanied by a change in the volume of that region, one may take the partial molar volume of the water phase, on scales larger than the size of pores, as being effectively zero. When either the internal diffusion or the surface evaporation is the dominant rate limiting process, simple models of drying result. Analytical solutions for both of these models have been obtained and extensively discussed in the literature.5, 22 Due to their inherent simplicity, and the presence of closed form analytical solutions for each model, these have widely been used in the fitting of the data from many drying experiments under a variety of circumstances.5 In fact, their popularity has been such that they have been considered even in situations where various assumptions inherent in the models, such as the requirement for a constant volume of the sample, have not been strictly valid. In such cases often an empirical effective diffusion coefficient, that is somewhat different to the real diffusion coefficient of water in the film, is often used in order to partially compensate for the shrinkage and other complications not present in the simple model.26

Where the changes in the volume of the film during drying are large, as would be the case if there are no stress-supporting structures formed by the solid fraction, the approaches discussed above can no longer be used. One immediate problem is that of specifying a reference frame against which the diffusion fluxes are measured. As was originally pointed out by Hartley and Crank27 there are many frames of reference that can be considered. For example one may specify the diffusion fluxes relative to the substrate side of the sample or to the film-air interface side. For a shrinking film these two frames result in different measured fluxes. Other possibilities have been considered involving mean mass, mean molar or mean volume reference frames.27, 28 So long as partial molar volumes of the components in the film are not composition dependent, then diffusion coefficients measured in one reference frame can easily be related to those obtained in another frame.29 Unless stated otherwise, in what follows it is assumed that the diffusion process and all the related diffusion coefficients are specified in the so called laboratory frame of reference, relative to the substrate.

There are two main factors that can contribute to changes in the volume of the sample. Firstly, the more obvious one associated with the loss of the moisture. However, provided the partial molar volumes of the components in the polymer solution are constant, independent of the composition of the solution, the problem simplifies greatly. Here the reduction in the volume remains strictly proportional to the amount of water that is lost at any stage throughout the drying process. This makes it simpler to determine the location of the moving air-film interface, knowledge of which is required for an analytical or indeed numerical solution to the drying problem. The second factor influencing changes in the volume of the film arises from the variation of the partial molar volumes of the two components with the mix ratio. This frequently occurs in problems involving inter-diffusion of two metals or metal oxides to form alloys.30 Variations arising as a result of changes in the partial molar volumes add a substantial degree of complication to the analysis of the diffusion process. Mathematical models of diffusion have been extended to account for these more complex cases in relation to metal couples.31 Of course in such problems, unlike drying, the total mass of the system remains a conserved quantity. This makes the use of constant mass reference frame a more appropriate choice.28 In the drying problem, this type of variation in the volume makes it that much more difficult to determine the location of the moving upper boundary. However, since this knowledge is crucial in obtaining a solution to the equations describing the drying process, the use of the constant mass reference frame is not as useful. A reference frame with respect to the substrate is preferable in this case. Fortunately in many practical situations involving the drying of food related biopolymer films, including systems studied here, the partial molar volumes remain reasonably constant over a wide range of mixture ratios. Nevertheless, since a theoretical analysis of changes arising from the variation of partial molar volumes has not been fully considered in the context of the drying of the biopolymer films, it is useful to first provide such a general treatment. The more familiar and widely studied cases, involving constant partial molar volumes, emerge then as special limits of this more general model. Before we present such an analysis, let us also first examine the evaporation of water from the upper surface of the film.

The conditions prevalent at the air–film interface determine the rate at which water evaporates from the film. These conditions include the nature of the solid phase, air temperature and flow above the film and the amount of moisture in the film just beneath the interface. For any given set of conditions there will be an equilibrium value of water content (molar concentration), *cweq*, in the film that will be in equilibrium with the moisture in the air above. Over a long period of time the water concentration in the film will approach *cweq* everywhere in the dried film. In general the rate of water loss per unit surface area of the film will be a function of (*cw*(*L*,*t*)  *cweq*), where *cw*(*L*,*t*) is the concentration of water on the surface at time *t* and *L* is the thickness of the film. The function can be expanded in powers of (*cw*(L*,t*) *cweq* ) and provided the difference between *c*(*L*) and  *cweq* is small, only the linear term needs to be retained.

 . (1)

The approximation remains a rather good one, even for relatively large values of (*cw*(L*,t*)  *cweq* ). The value of *K* captures all the temperature dependence and other factors related to the evaporation of the water from the film on the surface, but otherwise is a constant for a given set of conditions. It is known as the drying constant.22

 **3.1. Drying Limited by Evaporation.** If the diffusion of moisture is a relatively fast process in the film, then the only important factor in limiting the drying is the evaporation. This occurs for sufficiently small *K*, large water diffusion coefficient, *D*, and in thin films where *D*/(*KL*) >> 1. Under such circumstances the water concentration gradients are small across the film thickness. One may take the concentration of water as being uniform throughout the film *cw*(z,*t*) = *cw*(*L*,*t*) = *cw*(*t*), where *z* is the distance into the film as measured from the substrate. For cases with no shrinkage this leads to a very simple model that can readily be solved to give an exponential decrease in the concentration of water with time,32 *cw*(*t*) = *cweq* *+* (*cw*(0)  *cweq* )exp(-*Kt/L*) . Therefore let us consider the more interesting case where the thickness of the film decreases during the drying process. The basic equation to solve now becomes

 . (2)

The rate of shrinkage of the film, *dL*/*dt*, can be related to the rate of water loss from the film through the partial molar volume of the water, *Vw*, at any given time

  . (3)

We have indicated the possible dependence of *Vw*on the molar fraction of water in the mixture, ** *cw*(*t*) / (*cw*(*t*) + *cs*(*t*) ) , by writing this as *Vw*(**As the molar concentrations of water and the solid phases, *cw*(*t*) and *cs*(*t*), change with time, so will the value of ** and therefore *Vw*(** The total amount of solid phase in the film obviously will not alter. Therefore we also have

 . (4)

There is one further important relation that relates the values of *cw*(*t*) and *cs*(*t*) to each other, namely

 . (5)

Provided the variation of *Vw* and *Vs* with the water mole fraction ** *cw*(*t*) / (*cw*(*t*) + *cs*(*t*) is known, then in principle for any given value of *cw* the above equation can be solved to yield the corresponding value of *cs*. In practice of course the equation is non-linear, requiring a numerical solution or an approximate expression. Let us assume that for a particular system such an exact or approximate expression has been obtained, where *cs* = *g*(*cw*). Then, using eqs 3 and 4 to substitute for d*L*/d*t* and *L* in eq 2, we arrive at

  . (6)

Whether an analytical solution to the above differential equation can be obtained depends on the actual form of the functions *g*(*cw*) and *Vw* (**). Such a solution can be found for the early stages of the drying process, by linearising the functions around the initial value of *cw*. Another special but important case, involves systems for which *Vw* and *Vs* are constant. As mentioned before, many biopolymer solutions behave in this way, at least down to the very last stages of drying. For these systems it is easier to work with the volume fraction of water ** = *cwVw*. The volume fraction of the solid phase is then 1 ** = *csVs*. With partial molar volumes independent of the composition, function *g*(*cw*) = (1 *cwVw*) / *Vs* = (1 **) / *Vs*. Multiplying both sides of eq 6 by *Vw* we find

 , (7)

where **(0) is the initial volume fraction of the water in the film and *eq*isits equilibrium value. The above differential equation can be solved to give an explicit relation between time *t* and volume fraction of water ** in the system as follows:

 (8)

The results predicted by eq 8 is substantially different to that of the simple model not accounting for the film shrinkage, when *eq* and **(0) are not so small. However, for small values of these quantities i.e. *eq* << 1 and **(0) << 1, the equation predicts the same exponential behaviour

(*eq*) / **(0) - *eq*) = *exp*(-*Kt*/*L*(0) as the one obtained by the simple model. This is because at small values of *eq* and **(0), the term *cw*(d*L*/d*t*) becomes much smaller that *L*(d*cw*/d*t*) in eq 2, and hence the shrinkage of the film can be safely neglected. In the next section results obtained from eq (8) will be compared with our experimental data involving drying of casein and starch solution based films.

**3.2. General Model for the Drying Film.** In this section we will discuss the drying process in which diffusion, evaporation and shrinkage of the film are all significant and none may be ignored. The diffusion process has to satisfy a number of basic relations, the most obvious of which is the continuity equation for both the solid and the water phase within the film:

 , (9)

In eq (9) *ji* is the molar flux of component *i*, where suffix *i*=*w* or *i*=*s,* refers to the water or the polymer phases, respectively. Provided that the local equilibrium is also maintained at each point in the film, the concentrations of the two phases are also related to each other throughout the system. Once the composition ratio, ** is known at a point, then so are the values of *cw* and *cs* through equations

 , (10)

which is eq 5 now applied locally to each point *z*, and

 . (11)

Thus, it suffices to only focus on the diffusion of one component (e.g. water), since diffusion of the other component (solid phase) will simply follow suit. The relationship between *cw* and *cs* is a simple linear one for the cases where partial molar volumes are constant. This leads to the well known situation for which the diffusion coefficient of both components are identical, often referred to as the inter-diffusion coefficient.28, 29 To relate the diffusion of the two components in these more general cases, let us differentiate both sides of eq 10 with respect to *z*. We have

 . (12)

The above equation is obvious when *Vw* and *Vs* are composition independent, but it also holds more generally. This can be seen from the fact that

 . (13)

That the term in the bracket in the above equation is zero follows from the generalised form of Denham-Gibbs equation, valid for all partial molar quantities.33 It can easily be derived by considering changes in the volume of a uniform mixture of *nw* moles of water and *ns* moles of polymer solid phase and the fact that the volume, *V*, is a function of state. In other words ∂2V/(∂*nw*∂*ns*) = (∂*V*s*/*∂*nw*)*=*(∂*Vw/*∂*ns*).

A very similar argument can be applied to the derivative of eq (10) with respect to time to obtain

 , (14)

which in combination with the continuity equations, eq (9), may also be written as

  . (15)

Equations 9 to 15 apply quite generally to any two phase system, so long as the local equilibrium is maintained at each point throughout the system. They are valid irrespective of the laws that govern the dependence of the diffusion fluxes on concentrations. However, at this stage a choice has to be made with regards to the relations governing the dependence of diffusion fluxes on gradients of thermodynamic quantities. Several such laws have been suggested over a number of years of which Fick’s first law, Maxwell-Stefan’s law or Onsager’s flux law are amongst the best known and most widely used.28 In the present discussion it is assumed that the flux relation for the water phase, though not necessary the solid phase, can be described by Fick’s law

 . (16)

The symbol *Dw*(**) in the above equation denotes the compositional dependent diffusion coefficient of water, as measured in our chosen laboratory reference frame. It must be stressed that this is a phenomenological relation the validity of which has to be verified experimentally for the particular system of interest. Indeed, there are many situations, and in particular with regards to diffusion of water in glassy polymer films, where Fick’s law is not always obeyed.34-36 In other situations an equation similar to eq 16 can be developed only by redefining the length scale in a position dependent manner, and by expressing the concentrations in units consistent with this variable.27, 37 Substituting eq 16 into eq 9 for the water phase, leads to the familiar Fick’s second law

 . (17)

As the concentration of moisture evolves with time across the film thickness, the concentration of the solid phase, *cs*, has to follow suit in a manner dictated by eq 10 and 14. Since the aim is to eliminate all references to *cs* in the equations governing the drying process, we will consider the temporal variation of ** at each point, instead of *cs*. This is also useful as, more often than not, the experimental data for partial molar volumes are given as functions of the mole fraction of the constituent components. To obtain the required equation, we express *cw* in terms of ** using eq 10 and 11; *cw* = *****Vs* + *Vw* ]. Differentiating both sides of this equation with respect to time and rearranging we obtain

 .(18)

Equation 18 is particularly convenient for use in a finite difference or other similar numerical schemes26, 38, since (∂*cw*/∂*t*) is determined at each time step using eq 17. By updating the value of ** throughout the system the values of *Vw* and *Vs* can be refreshed at each point too.

Equations 17 and 18 have to be solved by imposing the appropriate boundary conditions to the film. At the bottom surface, in contact with the substrate, these are *jw*(0,*t*)*= js*(0,*t*)*=* 0, leading to

 . (19)

At the upper surface, where the evaporation of water takes place, one has

 . (20a)

for the water phase. The corresponding equation for the solid phase reads as follows:

 . (20b)

The rate of change of the film thickness is denoted by *dL*/*dt*. These conditions follow directly from eq 1 for the evaporation and the continuity equations for each phase at the air–film interface.

Multiplying eq (20a) by *Vw* and eq (20b) by *Vs* and adding the two together one obtains the rate of shrinkage of the film given by

 . (21)

The flux (*Vw jw + Vs js* ) in eq (21) above, when not equal to zero, indicates the presence of the so called Darken velocity39, 40 and the related Kirkendall effect41, 42 rather well known in the field of metallurgy. This effect manifests itself as a movement of marker non-diffusing entities relative to the substrate. From a theoretical view, the effect has been analysed in great detail in many different studies and has been the subject of several excellent reviews in the literature.37, 43 It suffices here to mention that for a system where the local equilibrium conditions are achieved quickly, and thus eq 10 prevails throughout the film, it can only occur if the partial molar volumes change with the mixture ratio. Conversely, the presence of the effect in a two component system where partial molar volumes are constant indicates that the two constituent components are not in local equilibrium with each other, at least in some regions in the system.

The reference to the solid phase can once again be removed from the above equation by expressing *js*in terms of *jw*. To do so we integrate eq 15 from 0 to a given height z into the film to obtain

 . (22)

With eq 22 substituted in 21, we finally obtain the required equation describing the shrinkage of the film purely in terms of the concentration and diffusion fluxes for the water phase:

 . (23)

Equations 16-18, together with the boundary conditions 19 and 20 and eq 23 for the rate of shrinkage of the biopolymer film completely describe the diffusion–evaporation process. Furthermore, they do so in a way that is fully consistent with the presence of local equilibrium, as imposed by eq 10 at each point. Using these equations, a numerical scheme can easily be implemented now to simulate the drying process. In such a scheme, it will be even more convenient if the integral term in the above equation could be reduced to a form which only involves local quantities at the air–film interface. We have not been able to obtain such an expression for the integral. The presence of this integral term in eq 23 reflects the fact that the shrinkage of the film depends on the changes in the mix ratio and thus those in the values of the partial molar volumes, occurring not only on the surface but throughout the whole of the film, all the way down to the substrate. Of course, when the partial molar volumes are constants, then no such considerations will arise and this non-local term should disappear. This is clearly the case in eq 23. We shall discuss the special case involving constant partial molar volumes next and show how the equations derived above take on their more familiar forms in such a circumstance.

**3.3. Systems Involving Constant Partial Molar Volumes.** When the partial molar volumes of the constituent components are not dependent on the composition ratio, the equations describing the drying process simplify significantly. In many biopolymers solutions this condition is satisfied quite well over a large range of composition mix ratios. It is only at the very last stages of the drying, where major changes in the structure of the film may occur, that the assumption begins to be violated. As we had done in the analysis of the case involving the drying process limited by evaporation, once again it is easier to work with the volume fraction of water, *= Vwcw*. Thus, multiplying both sides of eq 17 by *Vw* the moisture diffusion equation becomes

 . (24)

We now assume that the variation of the compositional dependent diffusion coefficient is provided in terms of ** rather than **. It is also immediately apparent that the diffusion equation for the evolution of the volume fraction of the solid phase (1**) is identical to eq 24, implying the expected result, *Dw*(**) = *Ds*(**). So long as the diffusion coefficients are given as a function of **, eq 18 is redundant and need not be considered further. The fact that the partial molar volumes are constant implies that the volume is now a conserved quantity in the problem. That is to say that the volume of the remaining film and that of the evaporated water together always equal the initial volume of the film. This requires

 . (25)

The above equation also results directly from eq 23 when *Vw* and *Vs* are constant, whereupon the integral term in the equation vanishes. Finally, the boundary condition 19 at the substrate side remains the same, while eq 20a at the air–film interface, *z* = *L*, can now be written as

 . (26)

The presence of a moving boundary condition in the problem is not desirable. It can be difficult to implement in a simple finite difference type numerical scheme and may require redefinition of the grid as the film shrinks relative to the grid size. This can be a source of numerical errors in the solution. One possible way to avoid such a problem would be to use a set of coordinate system, *y*, where the length scale is continuously redefined by the thickness of the film at time *t*:

 . (27)

In the new coordinate systems the air–water interface is always at *y* = 1. We also define **

 , (28)

such that

 . (29)

In terms of our new length scale, the diffusion coefficient becomes *D\** = *Dw*/(*L*(*t*))2, while the diffusion equation, eq 24, now turns into a diffusion-convection equation (see appendix A):

 . (30)

Numerically it is much more convenient to implement a solution to eq 30, which now has to be solved with a fixed boundary condition

 , (31)

at *y* = 1, rather than the moving boundary condition for eq 24. We have implemented a simple finite difference scheme to solve eq 30 in conjunction with eq 25. The solutions thus obtained will once again be compared to our experimental results once they are discussed in the next section.

# 4. RESULTS

## 4.1. The kinetics of Biopolymer Dehydration. The three biopolymer systems chosen for this investigation were done so for their very contrasting structures and properties. Casein and starch are both commonly used in industry in the formulation of edible films, though the films they form have vast differences. Casein forms a strong homogeneous protein network whereas starch, being a polysaccharide, has a more granular, brittle film structure prone to cracks and faults. A mixed system of casein and starch was also investigated to see if the addition of casein could help the film formation in polysaccharide based systems. The concentrations used were chosen so as to give similar viscosity and flow behaviour for all solutions.

Figure 1a-c show how the drying behaviour of sodium caseinate, starch, and sodium caseinate-starch mixed films respectively, changes under different conditions. The moisture ratio, Γ, defined as (*L*(*t*)φ(*t*) – *L*(∞)φeq)**/**(*L*(0)φ(0) – *L*(∞)φeq), was plotted against time. The quantities φt, φeq, and φ0 are the moisture content at time *t*, final equilibrium moisture content, and initial moisture content respectively, with *L* being the film thickness. In all cases, one can see that as temperature increases, the rate of drying also increases, as indicated by the more rapidly falling curves. This is because of two things. At higher temperatures, the water molecules within the film have more kinetic energy33, and thus can diffuse more quickly to the surface, where moisture loss occurs, resulting in a faster rate of moisture loss than that at lower temperatures. Secondly, an increase in temperature will also result in faster evaporation from the surface of the film. However, the effect of increasing the temperature is noticeably greater for the sodium caseinate system as compared to the starch and mixed systems. In particular, one should note that a temperature increase from 40 °C to 50 °C in the mixed system only results in a very small increase in drying rate, a behaviour that is different to both sodium caseinate and starch based systems. This suggests that the two components may have some sort of synergic interactions leading to networks that have a larger water holding capability.

Figure 1 – Plots of *Γ*= (*L*(*t)φ*(*t)*-*L*(∞)φeq)/(*L*(0*)*φ(0*)*-*L*(∞)φeq) against time for three systems at RH 30% a) 18 wt% sodium caseinate solution, b) 7 wt% starch solution, and c) 9 wt% sodium caseinate:4.5 wt% starch mixture solution at different temperatures ♦=30°C, ■=40°C, ▲=50°C

As expected, relative humidity also plays a role in the drying behaviour, as seen in Figures 2a-c. As relative humidity of the surrounding air increases, the rate of moisture loss decreases. An increase in relative humidity means that the surrounding air is more saturated and so the moisture gradient between the surface of the film and its surroundings is smaller, thus limiting the rate of moisture loss. However, below 30%, relative humidity has little effect on the drying of starch films, with the moisture ratio vs time curves at 20% and 30% relative humidity being almost identical to each other. At 40% relative humidity however, a slightly slower decline rate in moisture ratio is observed. This result suggests that for starch films, external relative humidity of the surrounding air plays a lesser role than the temperature dependence of the drying process. Conversely, changing the relative humidity conditions has more of an impact on the drying curves for the mixed system as compared to temperature.

Figure 2 - Plots of *Γ* against time for three systems at 30 °C a) 18 wt% sodium caseinate system, b) 7 wt% starch system, and c) 9 wt% sodium caseinate:4.5 wt% starch mixture system at different relative humidities ♦=20% RH, ■=30% RH, ▲=40% RH

It is constructive to examine the data in graphs of Figures 1 and 2 to see if a constant rate period and two distinct falling rate periods, often reported in the literature on drying of foods, can be identified here. This has been done in the graphs of Figures 3 and 4. Figures 3a-3c display the time variation of the drying rate for the three systems, at three different temperatures. The drying rate is calculated as (*W*n – *W*n+1)/*W*∞(*t*n+1 – *t*n), where *W*n is the weight of the film at the nth reading. i.e. the difference between two consecutive weight measurements, divided by the final weight and the time interval between the two. Data of this type, involving finite differences, are normally quite noisy and the results presented in Figure 3 are no exception in this respect. The graphs in Figures 4a-4c show the same data but now obtained at different values of air humidity. No clear constant rate period is evident in any of the cases presented here. In general for all graphs shown in Figures 3 and 4, the drying rate is fastest at the start of drying, dropping rapidly to a lower value later on as the process progresses further. This phenomenon was observed for all three systems and may suggest that the surface of the films are drying quicker than the bulk, thus resulting in the decrease in drying rate observed in Figures 3 and 4. Also it is evident that in all cases there appears to be no obvious transition between two distinct falling rate periods. These different drying regimes are assumed to be associated with different mechanisms of movement of moisture to the surrounding air.11, 12 In the constant drying period there is sufficient free water on the surface. The rate of drying is fixed in accord with eq 1, with the surface moisture concentration remaining constant at that for free water. Typically, during the falling rate period moisture is migrating through the bulk of the film to the surface, and the drying rate is decreasing with time. In the first failing rate this is in the form of liquid water. The second falling rate would occur when the surface is almost completely dry and dehydration involves evaporation of the partially bound water molecules and transport of the water vapour within the interior pores to the surface. However our systems do not exhibit any clear trends towards this behaviour. Therefore, if diffusion is the controlling factor in the dehydration process, it seems more appropriate to interpret the drying rate curves in terms of a changing diffusion coefficient, *D*, for water molecules, varying smoothly with the amount of moisture present at any point in the film. The continuously falling nature of the drying rate becomes even more pronounced as temperature decreases (Figure3) and relative humidity increases (Figure 4). Again, as highlighted in Figure 2b, the effect of relative humidity on the starch system is minimal.

Figure 3 - Drying rate vs. time graphs at 30% RH for a) 18 wt% sodium caseinate solution, b) 7 wt% starch solution, and c) 9 wt% sodium caseinate:4.5 wt% starch mixture solution at different temperatures ♦=30°C, ■=40°C, ▲=50°C

Figure 4 - Drying rate vs. time graphs at 30 °C for a) 18 wt% sodium caseinate solution, b) 7 wt% starch solution, and c) 9 wt% sodium caseinate:4.5 wt% starch mixture solution at different relative humidity values ♦=30% RH, ■=40% RH, ▲=50% RH

**4.2 Comparison of Theoretical and Experimental Data for Biopolymer Film Dehydration Process.** Mathematical models were constructed as described in the theoretical considerations section. Figure 5 shows three different curves simulating the dehydration process based on Fick’s second law of diffusion, as described by eq 17. In all these cases, it is assumed that the diffusion process is the limiting factor in determining the drying rate, with evaporation being rapid enough to maintain the surface moisture at equilibrium with the air above. The systems chosen are a) one with a constant diffusion coefficient and constant volume, b) with a constant diffusion coefficient, but involving film shrinkage as described in section 3.3, and c) a system with both a variable moisture dependent diffusion coefficient and film shrinkage. The diffusion coefficient for the two constant *D* cases was chosen to be 8.5 ×10–11 m2.s–1 , typical of that in solid food systems,5 such as vegetables. For the system with moisture dependent diffusion, the model proposed by Maroulis et al44 is used. This model itself is based on the analysis of a large number of reported experimental data in the literature. We chose *D* = 1.72×10–10 **×10–11**m2s–1, with the value of the diffusion coefficient half way through the drying process being roughly the same as that for the two constant *D* systems. In all three systems the initial moisture volume fraction was **(0) = 0.875, while the final equilibrium value **eq = 0.02. The initial thickness of the film was 4×10–4m. The data are presented as the reduced moisture ratio **= (**(*t*)*L*(*t*)  **eq*L*(∞))/(**(0)*L*(0)  **eq*L*(∞)) = (*L*(*t*)  *L*(∞))/(*L*(0)  *L*(∞)), plotted against the reduced time *t*/**, where the time scale ** = 4*L*(0)2/(2*D*). Plotted in this way, the results for all systems with constant volumes and a constant diffusion coefficient lie on a single master curve,39 irrespective of the values of *L*(0), *D*, **(0) and **eq. For systems where there is a variation in diffusion coefficient or film shrinkage, the initial values of *D* and *L* were used to calculate . Of course, in these latter cases the same universal scaling is not to be expected.

Figure 5 – Numerically calculated drying curves, showing **= (*L*(*t*)  *L*(∞)) / (*L*(0)  *L*(∞)) plotted against scaled time (2*Dt*/(4*L*(0)2), for diffusion limited dehydration. The graphs are for a) a system with constant *D* and *L* (dotted line), b) constant *D* and film shrinkage (solid line), c) with a moisture dependent water diffusion coefficient and shrinkage (dashed line). The inset shows the magnified graphs for the initial stages of drying.

While all three curves in Figure 5 follow similar trends, it is noticeable from the inset in the figure that the graphs deviate from each other very early on. In particular, the drying curve for the system with a constant *D* but film shrinkage (solid line) falls much more rapidly than the one that doesn’t involve a change in the film thickness (dotted line). This also means that our assumption regarding the diffusion being the limiting factor at the start of the film drying, might not apply throughout the whole process. As the film shrinks, the evaporation becomes increasingly the slower of the two processes, and hence the more dominant factor in controlling the loss of moisture. However, the effect can to some extent be compensated by the decrease in the water diffusion coefficient, as the moisture content of the film decreases. This is demonstrated by the dashed line of Figure 5, showing a faster drying than the one with a constant *D* and *L*, but slower than the system with constant *D* and variable *L*. It could well be then that in some practical cases, the effects of a reduction in *D* and a decrease in the film thickness largely cancel each other out. This allows the familiar analytical equation39 for the standard case to be fitted to the dehydration of such materials.

In Figure 6 we have attempted to scale all of our experimental drying data, obtained for different systems at various temperatures and humidity conditions, on to a single master curve. This is done by plotting moisture ratio ** against the scaled time *t*/** for each system, where **is an adjustable parameter chosen for each set of data to provide the best possible scaling. The data for different sets of systems, presented in Figures 1 and 2, all show a remarkably good level of scaling when plotted in this way. The only possible small discrepancy between the results arises towards the very last stages of the drying process, where we expect very contrasting behaviour for starch and casein based films. To us the good scaling of the data suggests that the drying process is either predominantly controlled by evaporation, where the time scale ***=L/K*, or else largely dominated by moisture diffusion, with **= 4*L*2 / (2*D*). If both factors were equally significant in the drying of our films, such scaling as that in Figure 6 would not be possible. One of the two processes is too fast relative to the other and therefore at best, only causes a small perturbation to the results otherwise obtained by its omission.

**Figure 6 – Experimental data of Figures 1 and 2, scaled on a single master curve. The solid line shows the best fit to the results using a numerically calculated diffusion dominated dehydration curve, with film shrinkage and a constant moisture diffusion coefficient.**

The time dependence of scaled experimental results indicates that moisture diffusion is unlikely to be the controlling factor. We have attempted to fit the scaled data in Figure 6 using numerically generated drying curves, obtained for systems where the evaporation is rapid and diffusion the controlling mechanism. Irrespective of whether the film shrinkage was taken into account or not, and the use of constant or moisture dependent diffusion coefficients, none of the results provided a good fit to the experimental data. The solid line in Figure 6 shows one such attempt, calculated for a system with constant *D* but decreasing thickness. The essential point is that for all of the diffusion limited drying curves the initial moisture loss follows a relation of the form (1** *~ *. In contrast, the experimental results are better described by (1** *~ t*. The poor fit to the experimental data, even in the best case, confirms that diffusion is not the limiting factor in the dehydration of these polymer films.

Following the above findings, the evaporation controlled case was considered. The simple exponential curve, obtained when the film shrinkage is neglected, results in a better fit to the experimental data at short times; . However, as clearly seen in Figure 7 (dashed line), the predictions grossly overestimate the remaining moisture content at longer times. With changes in the film thickness included in the analysis, the dehydration curve is described by eq 8. This equation does not admit a simple scaling relation between ** and scaled time *t*/**. Nevertheless if one considers a system where *eq* << **(0), as is the case here, then **(*t*)*L*(*t*) >> *eqL*(∞) for a considerable portion of the dehydration process. We can write (1*eq*) ≈ 1, *L*(∞) ≈ (1-**(0)*L*(0) and ** ≈ **(*t*)*L*(*t*)/(**(0)*L*(0)). With these approximations, eq 8, expressed in terms of ** now reads

 . (32)

For the initial stages of dehydration, where we have (1**) << 1, the above equation gives an identical result to the exponential curve, i.e. . At longer times, the shape of the curve is dependent on the initial moisture content. However, it turns out that all the systems we have studied here have a very similar initial moisture volume fraction. The caseinate based systems have a solid weight fraction of 18%. To convert this to a volume fraction value one needs the density of the caseinate in the solution. We obtained this by measuring the volume of a series of solutions, prepared with the same amount of water but different masses of added sodium caseinate. The density of sodium caseinate was found to be 1.53 gcm-3, in good agreement with reported values in the literature for relatively short protein chains.45 Using this value, the initial water volume fraction can be determined to be 0.875 for our caseinate solutions. A similar procedure for starch based systems gives the starch density as 1.35 gcm-3 and the initial water volume fraction as 0.9 for our solutions.

**Figure 7 – Comparison of the theoretically predicted drying curves for evaporation controlled dehydration with the experimental data. The solid line is for a model that includes the film shrinkage, while the dashed line represents the results for a model without shrinkage.**

We have calculated **(*t*), *L*(*t*) = (1-**(0))*L*(0)/(1**(*t*)) and hence , using eq 8 with an initial water volume fraction**(0) = 0.875 and a small final moisture volume fraction of 0.02. It is worth stressing that once the initial volume fraction of water is specified, the shape of the dehydration curve, ** vs. *t*/**, is entirely determined. There are no adjustable free parameters. The solid line in Figure 7 displays our theoretically determined dehydration results, with **= *L*(0)/*K*. The model gives a curve that fits the experimental data very well, indicating the important roles of evaporation and film shrinkage on one hand, and the relative insignificance of diffusion on the other. Nevertheless, even further modest improvement in describing the experimental data is possible if one does not entirely neglect the diffusion process. In Figure 8, we show the result of our numerical calculations, based on eqs 30 and 31, together with the experimental scaled master curve. The diffusion coefficient was chosen to be large but finite. The best fit was obtained when *D*/(*KL*(0)) ≈ 5.5. The excellent correspondence between the experimental and theoretical results is evident. Analysing the data using our model then, we find the evaporation constant *K* to lie between 1.2×10–7 ms-1, for casein at lower temperatures and large air humidity, to 3.6×10–7 ms-1 at higher temperatures, 40 °C, and low air humidity. With a film thickness of 0.4 mm, used in all our experiments, our best estimate for *D* is 5×10–10 m2s-1 for the diffusion of water in our biopolymer based films.



Figure 8 – The experimental data, all scaled onto to a single curve, compared with numerical predictions from a model combining evaporation with fast but finite diffusion, as well as film shrinkage. The inset shows the later stages of the drying process in more detail, with the gray line from fig. 7 also included for comparison.

# 5. CONCLUSIONS

In this work we have compared the dehydration in thin biopolymer films consisting of solutions of casein and starch, as well as those comprising of a mixture of the two. The two biopolymers chosen typify the two wide classes of macromolecules encountered in food systems, namely protein and polysaccharides. It is found that our dehydration curves as expressed by the moisture ratio plotted against time, studied under a range of air humidity and temperature conditions, can all be superimposed onto a single master curve, by a simple scaling of time for each system. We have shown that moisture diffusion dominated drying, whether involving a constant or a variable water diffusion coefficient, with or without film shrinkage, cannot accurately describe experimental dehydration curves obtained in this work. An analytical expression is derived for the moisture content in a film as a function of time, for a drying process in which the evaporation dominates and in which the film thickness decreases with the loss of moisture. This expression provides an accurate description of the experimentally obtained master curve, highlighting the crucial importance of accounting for the film shrinkage in theoretical calculations describing the dehydration process of such biopolymer films. The good correspondence between the experimental and the theoretical results also indicates the much more dominant role played by surface evaporation as compared to bulk diffusion. This to some extent is expected for thin films.

Situations where both evaporation and diffusion are equally important have also been considered. We have derived a generalised scheme for numerically solving such cases. Unlike most previous calculations, our scheme allows for the changes in the film thickness occurring as a result of the variation of local partial molar volumes with the evolving composition, as the drying progresses. This is in addition to the more usual shrinkage due to the loss of moisture. Under most circumstances the partial molar volume of water in systems of mixed water + biopolymer can be considered as almost constant. However, our main motivation for considering such a generalised situation has been to derive a set of equations applicable to the drying, even when the structure of the solid phase changes appreciably during the dehydration process. A particular example is when the solid phase in an initially fluid biopolymer solution begins to develop a stress supporting porous structure. In such a system the loss of water will no longer lead to the shrinkage of the film. This can be modelled by taking the effective partial molar volume as a composition dependent variable which approaches zero once a solid structure with a sufficient yield stress is formed. We intend to use this model in future to investigate dehydration in thin films where such changes in the structure of the biopolymer solutions are prevalent.

Application of the above model to the simpler case with constant partial molar volumes, under the condition where evaporation was the main limiting mechanism for the loss of water was studied. In these models the diffusion coefficient, *D*, was large but still finite, resulting in a slight perturbation to our analytical expression obtained by assuming *D* to be infinite. We found that in this case, the theoretical predictions of the model were in excellent agreement with the experimental data for the dehydration of our biopolymer films.

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**APPENDIX A**

We wish to express the diffusion equation, eq 24, in terms of a new set of variables *y*and ** as defined by eqs 27 and 28. This constitutes a continuous redefinition of the length scale, such that the unit of length is always the thickness of the film, *L*(*t*), at any given time *t*.

 We note that *L* is a function of *t* only*.* Therefore the right hand side of eq 24 can simply be written as

 (33) ,

with *D\** = *Dw*/*L*2. As for the left hand side of eq 24, we have

 (34) ,

where the subscript following each bracket indicates the quantity that is being kept fixed for that differential. Furthermore,

 (35) .

 Thus upon substituting eq 35 into eq 34 and equating the result with eq 33, we arrive at

  (36) .

Multiplying both sides of the above equation by *L,* and following a slight rearrangement, the required diffusion-convection equation, eq 30 is obtained. Although eq 30 is seemingly more complicated than the original diffusion equation, it is actually easier to implement numerically since now the condition imposed at the moving boundary *z*=*L*(*t*) becomes one at a fixed point *y*=1. This alleviates the need for re-meshing or redefining the grid size, as the film shrinks to a small fraction of its original size during the calculations. The presence of a convective term in eq 30 arise from the fact that a point at a fixed height *z* from the substrate, now moves with a velocity –( *y*/*L* )(*dL*/*dt*) in the newly defined *y* coordinate system.

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**Notes**

The authors declare no competing financial interest.

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