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## Measurement of the effective diffusion coefficient of water in spray dried amorphous lactose particles

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### Abstract

Stickiness and caking phenomena in dairy powders have been attributed to the amorphous lactose component in dairy powders. The effect of water on the glass transition temperature of amorphous lactose is a key to understanding these phenomena. The speed at which the powder particles take up water is critical when modelling caking or sticking processes. There is little in the literature on the measurement of this. This paper presents a method that uses the absorption of water vapour into a monolayer of particles of mixed size to estimate the diffusion coefficient of water in amorphous lactose. The aim was to measure the diffusion coefficient of water in amorphous lactose. Amorphous lactose particles were produced by spray drying and freeze drying and residual free moisture removed by further drying in an oven at 105 °C. A monolayer of the particles was spread over a Petri dish and the dish exposed to 30 % RH air at 30 °C. The change in weight with time was recorded. The particle size distribution was measured using a Malvern Mastersizer S. The size distribution was combined with a mathematical model for the absorption of water into a sphere, applied to each particle size simultaneously, to estimate the weight increase with time. The diffusion coefficient that minimised the sum of squares of the difference between the predicted and experimental values was taken as the diffusion coefficient of water in amorphous lactose. The diffusion coefficient of water in amorphous lactose was found to vary depending on how the particle was made. Values were  $(3.4 \pm 1.7) \cdot 10^{-14}$  and  $(6.6 \pm 0.7) \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$  when made by spray drying from 30 wt% and 10 wt% solutions respectively, compared to  $(4.5 \pm 2.5) \cdot 10^{-11} \text{ m}^2 \text{ s}^{-1}$  for freeze dried particles. This result indicates that the diffusion rate into amorphous lactose occurs faster than previously thought in freeze dried products.

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*Keywords:* glass transition temperature; crystallization; amorphous lactose; effective diffusion coefficient

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## 1. Introduction

Amorphous lactose is produced when dairy powders are dried quickly, such as when milk powders are produced by spray drying or when lactose crystals are flash dried after the centrifuge. Amorphous lactose when it exceeds its glass transition temperature has been shown to be the major cause of stickiness and caking during production of dairy powders [1-4]. The glass transition temperature is a strong function of the moisture content of the powders and they are known to be very hygroscopic. What is not known is how quickly these particles will take up moisture from the atmosphere. Only one estimate of the diffusion co-efficient of amorphous lactose was found in the literature. This value was  $2.33 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$  for spray dried lactose.[5].

The obvious way of measuring the diffusion coefficient of amorphous lactose is to measure the rate of weight increase with time into a mono layer of equal sized amorphous lactose particles and then to use the standard diffusion models into a sphere to find the diffusion coefficient. However, it is very difficult to produce evenly sized amorphous lactose particles. After many attempts to do this, it was decided to abandon that approach and to instead look at how we could change the absorption model to fit what we could easily produce in the way of particles. The approach was to produce some amorphous lactose, both by spray drying and by snap freezing followed by freeze drying, and then to measure the particle size distribution of the particles and then model the absorption into the complete range of particles with time, realising that the small particles will approach equilibrium much quicker than the larger particles.

This paper details the experimental and analytical method used to measure the diffusion coefficient of water in spray dried and freeze dried amorphous lactose and presents the results obtained.

### Nomenclature

D	the diffusivity of water in amorphous lactose	$\text{m}^2 \text{s}^{-1}$
R	the radius of the sphere	m
t	time	s
$Y_{ac}$	Fraction accomplished change	

## 2. Materials & Methods

The full details of the methods are given by [6] and a summary only is presented here.

Amorphous lactose particles were produced by either spray drying 10 and 30 wt% solutions, made from pharmaceutical grade lactose and distilled water, in a GEA Niro pilot plant spray drier using the inbuilt two fluid nozzle spraying upwards with the inlet gas temperature at 200 °C and the solutions applied at a rate to keep the outlet air temperature at 85 to 94 °C, or by using a droplet generator (MicroFab MJ-ABP-01-80-6MX droplet generator with an 80 µm orifice diameter and a 50 µm orifice diameter droplet generator produced by University of Melbourne) to spray a 10 wt% lactose solutions into liquid nitrogen. These frozen particles were freeze dried in a freeze drier model FD18LT “ISLA” from Cuddon LTD. Blenheim in New Zealand, at -40 °C and -1 mbar pressure, which was the limit of the freeze-dryer.

The size distribution of the particles was measured using a Malvern Mastersizer S laser scattering particle size analyser. The samples were dispersed using the Small Volume Sample Presentation Unit. Isopropanol supplied by Biolab (Aust) Ltd was used as a dispersant. The applied refractive index for

lactose is 1.5330 and for isopropanol 1.3800. The dial for the stirrer of the sample unit was set to 1 o'clock. The 300RF lens covering a range from 0.05  $\mu\text{m}$  to 878.7  $\mu\text{m}$  was used and the analysis model chosen was polydisperse.

The size distribution was then combined with a mathematical model for absorption of water into a sphere [7, 8]:

$$Y_{\text{acc}} = 1 + 2 \sum_{j=1}^{\infty} (-1)^j \frac{j^2 \pi^2 D t}{R^2} \quad (1)$$

to estimate the weight increase with time. In Equation (1) is  $D$  the diffusivity of water in amorphous lactose and  $R$  the radius of the sphere. Equation (1) represents the concentration profile at the centre of the sphere. Using equation (1) the fraction accomplished change was calculated for each standard size class of the Malvern Mastersizer S using the mean value of each size class as sphere radius. The total accomplished change  $Y_{\text{tot}}$  was then calculated by means of equation (2):

$$Y_{\text{tot}} = \sum_j v_j Y_{\text{acc}j} \quad (2)$$

where  $v_j$  is the volume fraction and  $Y_{\text{acc}j}$  the fraction accomplished change of size class  $j$  respectively. The diffusivity  $D$  that minimised the sum of squares of the difference between the predicted weight and the experimental value was taken to be the diffusion coefficient of water in amorphous lactose.

The diffusion experiments consisted of placing a mono layer of amorphous lactose particles on the bottom of a Petri dish in a dry environment and then covering the dish while it was transferred to the scales. A Mettler AE 200 scale was placed in a controlled RH and temperature environment, and at time zero the lid was lifted and the weight was recorded with time using an Agilent 34970A data logging system connected to an Intel® Pentium® 4 PC with Windows XP Professional as the operating system via an RS232 interface. The apparatus is shown in Figure 1.

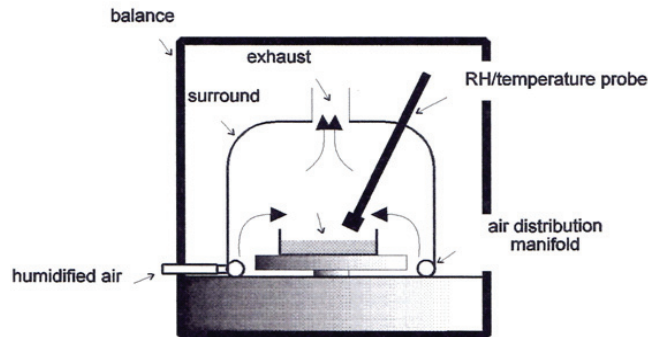


Fig. 1. Sorption rate measurement equipment

### 3. Results & Discussion

The particle size distribution measurements were conducted using two dispersants; namely pure isopropanol and isopropanol that had been saturated in lactose. Both dispersants showed that the amorphous lactose was more soluble than lactose monohydrate crystals with the obscuration level falling

with time and then a new larger size developing as a lactose crystal was formed. This is shown in Figure 2.

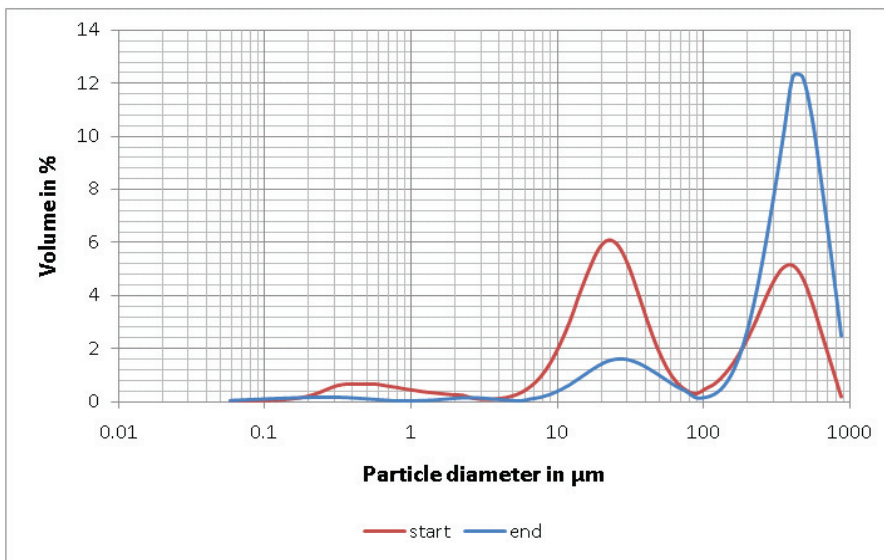


Fig. 2. Change in particle size distribution when leaving the amorphous lactose in isopropanol in the Small Sample Presentation Unit of Malvern Mastersizer S

Figure 3 shows 3 repeat runs with the 2 dispersants with readings being taken as soon as possible after adding the sample. These runs show that there was no significant difference between the two dispersants, so pure isopropanol was used for the rest of the runs. Figure 3 also shows a peak at the 200 μm level. This has been attributed to agglomeration of the smaller particles produced by the spray in the spray drier during the sieving operation.

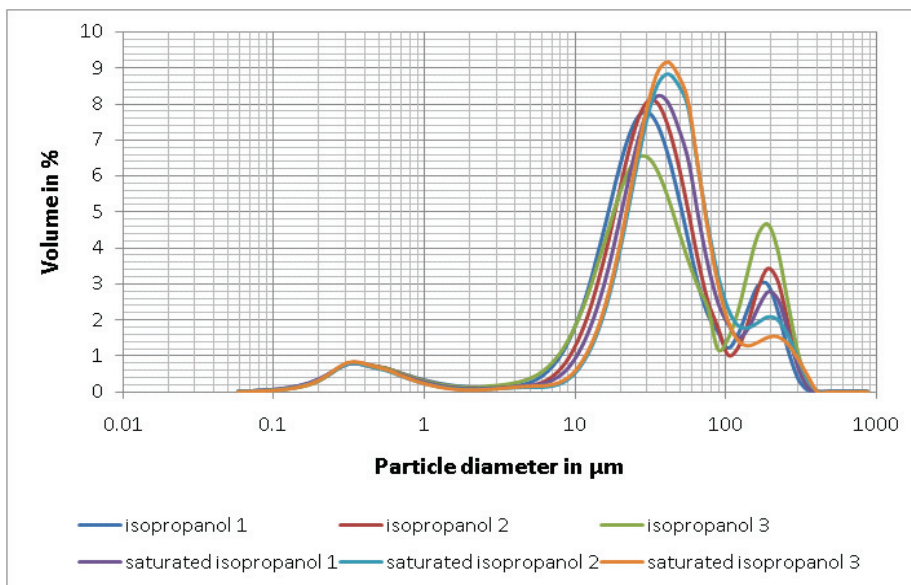


Fig. 3. Particle size distributions of monolayer particles for batch 8 of the spray drier 30 wt% lactose solution after having been sieved with a 250 μm test sieve.

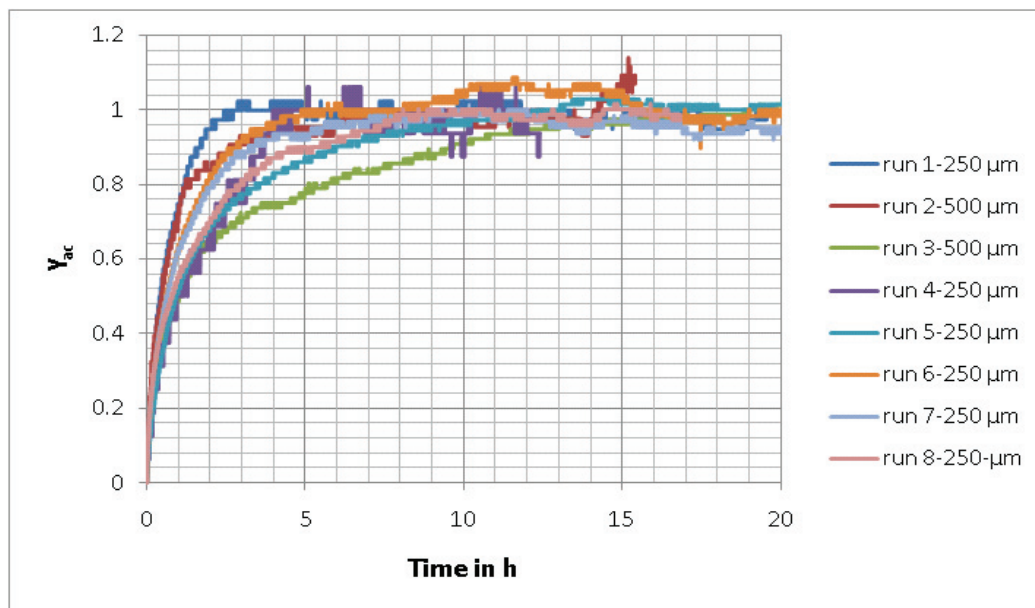


Fig. 4. Monolayer moisture sorption runs using the Fines of batch 8 – produced from a 30 % w/w lactose solution:  $Y_{ac}$ ...fraction accomplished change

Figure 4 shows the results of 6 replicate experiments with particles sieved with the 250  $\mu\text{m}$  sieve and 2 with the 500  $\mu\text{m}$  sieve. There is quite a bit of variation in the results. This has been attributed mainly to the experimental error in the weighting and the resolution of the balance (0.1 mg) when the weight changes were as low as 1.6 mg over the experiment. Other factors such as changes in the relative humidity and temperature might also be contributing, although in most runs the temperature fluctuations were within  $\pm 0.22$   $^{\circ}\text{C}$  and the RH within  $\pm 0.5\%$ . The fluctuations were found to be within the experimental errors when calculating the diffusion coefficients as will be seen in Table 1.

Figure 5 shows the fitted results when the whole particle size distribution was used to model the absorption into a mono layer of spray dried amorphous lactose particles made from a 30 wt% solution and sieved with a 250  $\mu\text{m}$  sieve. (Run 5 in figure 4.) The diffusion coefficient that minimised the sum of squares of the errors was  $1.07 \cdot 10^{-13} \text{ m}^2 \text{ s}^{-1}$ . It is obvious that the model does not fit the data very well, with it predicting faster absorption at the start and slower towards the end when compared to the experimental data. It appears that the larger particles in the distribution are equilibrating faster than the model predicts. This could well be the case if the larger particles are made up of agglomerations of smaller particles as suspected in the particle size distribution. The manufacturers of the spray nozzle say that the maximum size of droplet produced should be 90  $\mu\text{m}$ . The agglomeration was confirmed by viewing the particles under a microscope.

The model was re-run using only the particle size distribution for particles below 89  $\mu\text{m}$  and Figure 6 shows that a very good fit was obtained. The diffusion coefficient was found to be  $2.35 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$ .

Table 1 shows the results for the spray dried and freeze dried amorphous lactose particles. There was a significant difference between the diffusion coefficients for the two methods of producing amorphous lactose. The spray dried lactose from 30 wt% and 10 wt% solutions had diffusion coefficients of  $(3.4 \pm 1.7) \cdot 10^{-14}$  and  $(6.6 \pm 0.7) \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$  respectively, compared to the freeze dried samples with a diffusion coefficient of  $(4.5 \pm 2.5) \cdot 10^{-11} \text{ m}^2 \text{ s}^{-1}$ . This difference has not been seen in the literature as the only value found was  $2.23 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$  for spray dried amorphous lactose made from a 12.47 wt% solution[5].

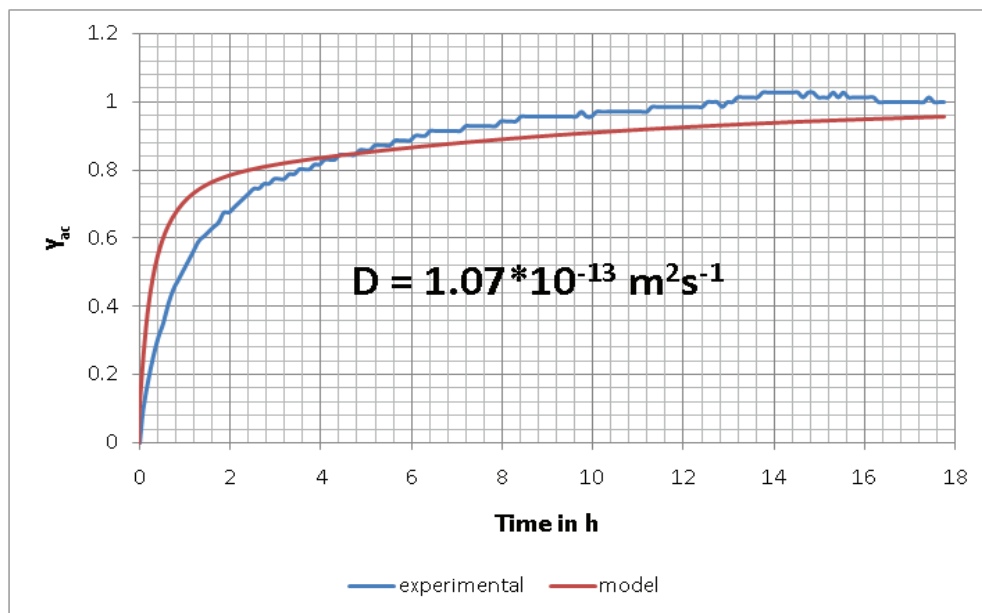


Fig. 5. Comparison of fitted and experimental diffusion time of run 5 of Figure 4 taking the complete size distribution into account

The difference between the spray dried and freeze dried samples is to be expected when one considers the processes that the particles undergo during production of the amorphous lactose. For the freeze drying process the particles were snap frozen in liquid nitrogen and then freeze dried with the water being sublimed off leaving a very open and porous structure. However, during the spray drying process, water is evaporated off from the droplet that is sprayed into the drier. During this process the droplet shrinks until the point is reached where the particle becomes dry enough that the viscosity at the surface becomes high enough so that the particle stops shrinking. This produces a particle that is much denser and less porous than that produced by the freeze drying process and this is reflected in the much higher diffusion coefficient for the freeze dried amorphous lactose.

Table 1. Fitted diffusion coefficients for amorphous lactose particles produced by spray drying 30 wt% and 10 wt% solutions and by freeze drying droplets from 20 wt% solutions

Run	Spray dried 30 wt%	Spray dried 10 wt%	Freeze dried 20 wt%
1	6.58E-14	6.97E-14	1.50E-11
2	5.56E-14	6.54E-14	2.75E-11
3	1.80E-14	6.77E-14	7.87E-11
4	2.62E-14	7.26E-14	5.10E-11
5	2.35E-14	5.39E-14	5.17E-11
6	3.29E-14		
7	2.91E-14		
8	2.14E-14		
Mean	3.41E-14	6.59E-14	4.48E-11
Standard deviation	1.73E-14	7.19E-15	2.46E-11

student t test was conducted between the means for the two spray dried products and it showed that at the 99.7% level of confidence, the two means were significantly different with the diffusion coefficient for amorphous lactose produced from the 30 wt% lactose solution being significantly lower than that from the 10 wt% solution.

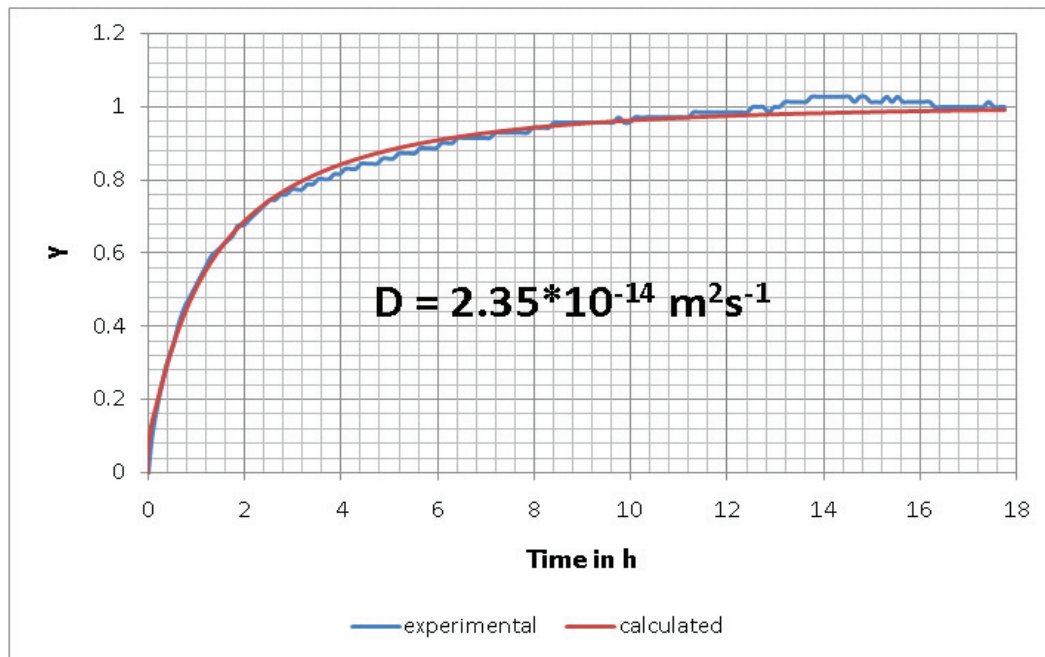


Fig. 6. Comparison of fitted and experimental diffusion time of run 5 of Figure 4 taking only the size distribution of particles below 89  $\mu\text{m}$  into account

#### 4. Conclusion

The diffusion co-efficient of water in amorphous lactose was found to vary depending on how the particle was made. Values were  $(3.4 \pm 1.7) \cdot 10^{-14}$  and  $(6.6 \pm 0.7) \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$  when made by spray dried from 30 wt% and 10 wt% solutions respectively, compared to  $(4.5 \pm 2.5) \cdot 10^{-11} \text{ m}^2 \text{ s}^{-1}$  for freeze dried amorphous lactose particles made from 20wt% solutions. This result indicates that the actual effective diffusion rate into amorphous lactose actually occurs faster than previously thought in freeze dried products.

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