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Probing composition and molecular mobility in thin spherical films using nuclear magnetic resonance measurements of diffusion

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Abstract

The composition and molecular mobility within thin spherical liquid films have been investigated using nuclear magnetic resonance (NMR) diffusion measurements. These films were formed either on the surface of pores inside a sponge at low saturation or by adsorbed water on the outside of urea prills during caking. Using pulsed field gradient (PFG) NMR experiments, the molecular mobility within these liquid films was determined through analysis of the conditional probability density for displacement (propagator). Molecular diffusion coefficients were determined for films in the sponge and prill systems by fitting the experimental propagators using a model for diffusion on an array of isotropically distributed infinite planes. By comparing these diffusion coefficients with bulk diffusion coefficients for a range of concentrations of urea solutions (2.1 M, 6.2 M and saturated), it was possible to optimize the PFG experimental parameters to enable accurate determination of molecular diffusion in these spherical liquid films. Determination of the diffusion coefficients for a range of urea solutions in the sponge enabled identification of the composition of the film that formed on the surface of the urea prills. Analysis of these data showed that the liquid layers are composed of saturated urea solution covering the surface of the prills, with an estimated layer thickness of the order of 10^{-5} m. The shape of the propagators indicated the adsorbed water was uniformly distributed over the surface of the urea prills, rather than primarily in the meniscus between particles, which agrees with dye visualisation experiments on a pair of urea prills during caking. This work provides the first quantitative measurements of diffusion in thin spherical films, which is a key parameter for determining what controls the presence and rate of bonding between adjacent particle surfaces.

1. Introduction

The characterization of the thickness, composition and mobility of molecules within spherical thin films is of importance in a range of chemical engineering environments such as multiphase flow and surface wetting in porous media, foams and encapsulation. This information is of particular interest in understanding the molecular processes involved in the formation, and consolidation over time, of solid bonds between particles, which is known as caking. This is a widespread issue in the

processing of powder feed materials in the food, chemical and pharmaceutical industries, which can result in reduced flowability and processability of these materials. This is particularly a problem for amorphous water-soluble solids, such as salt, sucrose or urea, where caking has been linked to the adsorption of water from the surrounding ambient air when stored at high relative humidity[1-5]. In these materials, the solid particle partially dissolves in the adsorbed liquid, forming a thin layer of solution on the surface and a liquid bridge at the contact point between particles. When the relative humidity is lowered again, the liquid bridge dries out and the dissolved material crystallizes as a solid bond between the particles[6, 7]. Models that describe the solid bridge formation, based on evaporation of liquid layers, often include a diffusional term describing the motion of solute molecules towards the crystal surface. Therefore, detailed knowledge of the solute diffusion coefficient in the liquid is crucial in modeling the caking process of water-soluble solids[8, 9].

Previous investigation of the diffusivity of solutes in non-evaporating thin liquid films have employed infrared spectroscopy[10] and surface impedance spectroscopy[11]. These studies revealed lower diffusion coefficients in the films than in bulk solutions. However, studies on the formation of solid bonds between spherical particles during caking have not focused on the molecular mobility within the thin liquid films on the surface of these particles. Models assume that molecules have similar diffusion coefficients in the thin film as they do in the bulk and no measurements of diffusion coefficients in systems of wet spherical particles have been reported in the literature. Yet, knowledge of the diffusivity of solutes in thin films is important for characterizing the formation of solid bonds and hence predicting the caking strength of bulk solids. A primary aim for this paper is to address this gap in knowledge and to provide quantitative information on molecular mobility, and chemical composition, within the thin fluid layers formed on the surface of spherical urea particles during caking.

Recent work on the caking behavior of prilled urea has shown that urea adsorbs a large amount of water vapor when stored close to its critical relative humidity at a given temperature[12]. The adsorbed water is observed to form a liquid meniscus between particles. It is believed that urea dissolves into the liquid until saturation is reached. This liquid bridge is then transformed into a solid one over a period of time, dependent on the rate of mass transport from the prill surface into the bridge[13]. This process is assumed to take place through diffusional transport within a thin layer of urea solution on the surface of the prills. To characterise correctly these mass transfer rates, it is important to determine the diffusivity of urea in the liquid layer surrounding the particles.

Nuclear magnetic resonance (NMR) pulsed field gradient (PFG) experiments are able to non-invasively measure the displacement of molecules containing NMR active nuclei (such as ^1H). These experiments produce average self-diffusion coefficients, D, as well as one-dimensional probability densities of displacement P(Z,Δ) (known as propagators) along the direction of the applied gradient (z) over an observation time Δ.[14] For unrestricted bulk diffusion, propagators have a Gaussian shape, with the full-width-at-half-maximum (FWHM) corresponding to $\sqrt{2D\Delta}$. Propagator measurements have been successfully used to investigate the distribution and mobility of fluids in numerous porous media[14, 15]. In a paper by Holmes et al.[16], propagator experiments were used to investigate molecular diffusion within surface-wetting films in a water-

wet sandstone containing mixtures of brine and dodecane. In their paper, the propagators for water, at low water saturations, were found to deviate from bulk (Gaussian) behaviour, highlighting the restricted motion of the water in thin layers on the surface of sandstone's spherical cavities. By modeling the film as an isotropically oriented array of unconnected planes, they were able to fit the experimental propagators and determine the planar diffusion coefficient, D_p, of the water. In these experiments D_p was found to vary with observation time, which at the time prevented a quantitative determination of diffusion coefficients in that system.

In this paper, we use dye visualisation and NMR PFG experiments to study liquid films that form on the surface of urea prills during caking. These films form when water is adsorbed on to the surface of the prills, from the atmosphere, which then dissolve some of the solid urea. Molecular diffusion within these thin spherical films was observed as a function of observation time (Δ) and diffusion coefficients were determined by fitting propagators by modeling the system as an isotropically oriented array of unconnected planes. The resulting diffusion coefficients were compared with diffusion coefficients determined for a range of urea solutions, in bulk and as thin films on the surface of pores inside a sponge of comparable pore dimensions to the urea prills. By comparing these data, it was possible to optimize the PFG experimental parameters to allow accurate determination of the composition and diffusivity of molecules within thin spherical films formed inside the sponge pores and on the outer surface of the urea prills.

Pulsed field gradient (PFG) measurements of molecular displacement
PFG measurements use a pair of magnetic field gradient pulses, of width δ, amplitude G and separation Δ, to impart a phase shift in the NMR signal, which is dependent on the displacement, Z, along the direction of the gradient during Δ [14]. PFG experiments typically measure the signal, S(G), as a function of gradient strength In systems of short T_2 relaxation times, as is often the case for fluid within porous media, pulsed gradient stimulated echo (PGSTE) sequences are frequently employed[14], which are less sensitive to T_2. By fitting the normalised signal, S(G)/S(0), to the Stejskal-Tanner (ST) equation[17] (Equation 1), the self-diffusion coefficient D is determined.

$$S(G)/S(0) = \exp[-\gamma^2 G^2 \delta^2 D(\Delta - \delta/3)] \qquad \text{(Equ. 1)}$$

Alternatively, Fourier inversion of S(G) with respect to $\boldsymbol{q}_z$ (where $\boldsymbol{q}_z = \gamma \boldsymbol{G}\delta/2\pi$) produces the averaged propagator, P(Z,Δ), which describes the probability that spins will displace a distance Z over the observation time Δ[18]:

$$S(\Delta, \boldsymbol{q}_z) = S(0) \int_{-\infty}^{+\infty} P(Z, \Delta) \exp(-iq_z Z) dZ \qquad \text{(Equ. 2)}$$

In cases where diffusion occurs in thin layers on a surface, the shape of the propagator deviates from that of a Gaussian, as found in bulk diffusion. In the investigation by Holmes et al.[16], the molecular displacement of water in thin layers on the surface of spherical pores, within a water-wet sandstone, resulted in a more pointed propagator, with steeper sides, which they described as having a cusp-like shape. These thin layers were modeled as an isotropically-oriented array of unconnected planes. By

neglecting the effects of diffusion perpendicular to the film, they simplified the expression for the two-dimensional propagator for each plane and then projected it onto the gradient axis and averaged over all plane orientations to obtain the following one-dimensional propagator expression:

$$P(Z,\varDelta) = \sqrt{\frac{\pi}{4D_p\varDelta}} erfc\left(\sqrt{\frac{Z^2}{4D_p\varDelta}}\right) \qquad \text{(Equ. 3)}$$

where D_p is the planar diffusion coefficient and *erfc* is the complementary error function. Using this model, they were able to fit the experimental propagators and determine D_p. Then by simulating diffusion on spheres and comparing the resulting propagators with those produced by the infinite planes model, they were able to determine the range of validity for the model and the relation between D_p and the diffusion coefficient on the spherical layer, D_s. Their calculations, for a variety of sphere radii (R) and observation times ($\varDelta$), indicate that for $D_s \varDelta / R^2 \leq 0.2$, the relation between D_p and D_s can be well represented by equation 4.

$$D_p = D_s(1 - \frac{\varDelta}{R^2}D_s) \qquad \text{(Equ. 4)}$$

Holmes et al. however, found that the experimental planar diffusion coefficients D_p, and hence the calculated D_s, were dependent on $\varDelta$. This observation highlighted two limitations of the infinite planes model. Firstly, that at very short observation times, the displacement of molecules is not significantly restricted by the thin layer, and secondly, that at long observation times the diffusion molecules also experiences the curvature of the sphere. In a subsequent work, the authors[19] also found that the thickness of the liquid bridge between spherical particles had an effect on the shape of the propagators, introducing a Gaussian component that can prevent the use of the infinite planes model. This effect was shown to be important only in the case of highly wet systems and is therefore expected to play a negligible role in the present study, where water saturation is low.

2. Experimental and methodology

2.1.   Sample preparation

The urea prills (BASF) were of technical grade and free from any additives, with a spherical shape and diameter of 1.6 - 1.7 mm. Bulk urea solutions were produced by dissolving the urea prills in de-ionised water, at a range of concentrations from 2.1 M to a saturated solution (ca. 10.5 M at 24 ˚C). Synthetic foam sponges, with average pore diameters of 1 - 2 mm, were cut into plugs of 10 mm diameter and 50 mm length. Sponges were then filled with distilled water or urea solution (2.1 M, 6.2 M or saturated), before excess liquid was removed by shaking.

Sponges and prills were inserted into the NMR spectrometer in 10 mm NMR tubes. The sample length exceeded that of the observable region of the radiofrequency coil, to eliminate any end-effects. The urea prills were maintained at a relative humidity of 75.5 ± 0.3 % by including a saturated sodium chloride solution[20] at the bottom of a

sealed tube. All experiments were performed at 24 ± 0.1 °C and repeated a minimum of three times.

2.2. Dye propagation on urea prills

Two contacting urea prills were clamped between two fixed pins and stored at 24 ± 0.2 °C and 75.3 ± 0.8 % RH, in a climatic glove box[13]. Basovit Patentblue E131 colourant (85%, BASF SE) was used to visualize diffusion during the caking process. A brush hair was used to apply the colorant on the prill surface. Liquid bridge formation and colourant propagation were observed by video recording over time with a CDD camera that allowed the magnification and focus to be controlled without opening the glove box. A more detailed description of the experimental set up can be found elsewhere[13].

2.3. NMR measurements of bulk diffusion and propagators

All ^{1}H NMR experiments were performed on a 7 T Bruker DMX300 spectrometer operating at proton resonance frequency of 300.13 MHz with a 25 mm radiofrequency coil. PGSTE measurements were performed using a magnetic field gradient in the z direction (which is vertical and parallel to the orientation of the NMR tube), with 64 gradient values (going from – G_{max} to + G_{max}) and 16 averages. PGSTE values of $\{\Delta = 50$ ms, $\delta = 3$ ms, $G_{max} = 0.6$ T m$^{-1}\}$; $\{\Delta = 100$ ms, $\delta = 3$ ms, $G_{max} = 0.5$ T m$^{-1}\}$; $\{\Delta = 200$ ms, $\delta = 3$ ms, $G_{max} = 0.4$ T m$^{-1}\}$; $\{\Delta = 400$ ms, $\delta = 3$ ms, $G_{max} = 0.3$ T m$^{-1}\}$ were used, which ensured a signal attenuation of S(G)/S(0) ≤ 1 %). Diffusion measurements on the prill system were made 1 and 72 hours after the sample was set-up.

A weighted-average diffusion coefficient was determined for each bulk solution, by fitting the echo amplitude (S(G)/S(0)) to the Stejskal-Tanner equation (equation 1). Separate diffusion coefficients for water and urea were determined by Fourier transforming and phasing each spectrum, then fitting equation 1 to the integral of each peak, as a function of G. The NMR signal for the urea solutions had a significantly shorter T_2* in the sponge and prill systems, compared to the bulk, hence, it was not possible to distinguish between water and urea signals due to increased line-broadening. Thus, propagators P(Z,Δ) in the sponge and prill systems were weighted-averages of the water and urea molecules. These averaged propagators P(Z,Δ) were determined from the PGSTE data by Fourier transformation of the echo amplitude with respect to q_z. The resulting propagators were then fitted to the infinite planes propagator model (equation 3) to determine D_p. For all experiments presented in this work $D_s \Delta / R^2 \leq 0.01$ for $D_s < 10^{-8}$ m^2 s^{-1}. Hence, the condition $D_s \Delta / R^2 \leq 0.2$ is largely met and equation 4 can be used to determine D_s. Note that this also means that, for the range of parameters used in this work, $D_s \approx D_p$ since $D_p / D_s = (1- D_s \Delta / R^2) \approx 1$.

3. Results and discussion

The propagation of dye on a pair of urea prills is shown in Figure 1. At a relative humidity of 75.5 %, a liquid bridge formed at the contact point between the particles (Figure 1a). Within less than 1 hour, a stable bridge diameter was reached that stayed

constant over time. Following application, the colourant spread within the water film on the prill surface by mutual diffusion (Figure 1a-b). After 1 minute (Figure 1c), the whole particle was colored in blue and the colorant passed through the liquid bridge to the neighboring prill. This rapid propagation of the colourant on the particle surface suggests the presence of a continuous liquid film, not only at the bridging point but all over the prill surface. The dark blue veins indicate that due to surface roughness and elongated cavities between the crystal grains, the liquid film does not have the same thickness all over the prill surface. After 30 min, such surface irregularities become less visible as the colorant is more evenly distributed around the prill (Figure 1d).
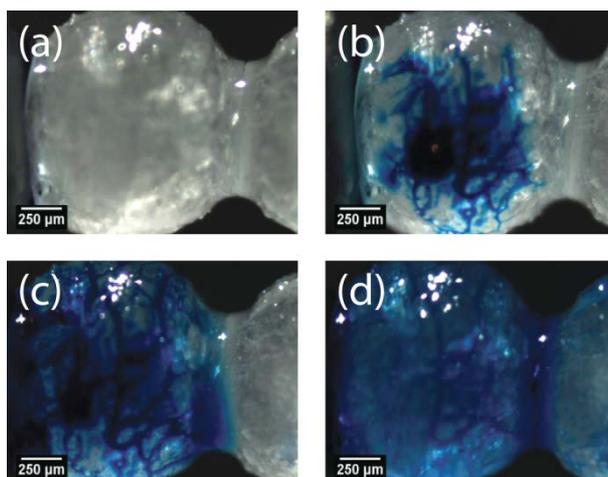

Figure 1. Images showing dye propagation on the surface of caking urea prills, 24 °C and 75.3 % RH (± 0.2 °C, ± 0.8 %). (a) Image acquired 30 minutes after prills have achieved steady-state and a bridge is formed, prior to dye application. (b)-(d) Images acquired immediately after (a), 1 minute after (c) and 30 minutes after (d) dye application. The red dot on image (b) corresponds to the dye application point.

Figure 2 shows a plot of the diffusion coefficients of water and urea in bulk, with their weighted average, for different urea concentrations up to a saturated urea solution ([urea] = 10.5 M). These results show that an increase in urea concentration causes a decrease in both water and urea diffusion, due to an increase in solution viscosity. The obtained values for urea diffusion are in good agreement with previously reported values[21].
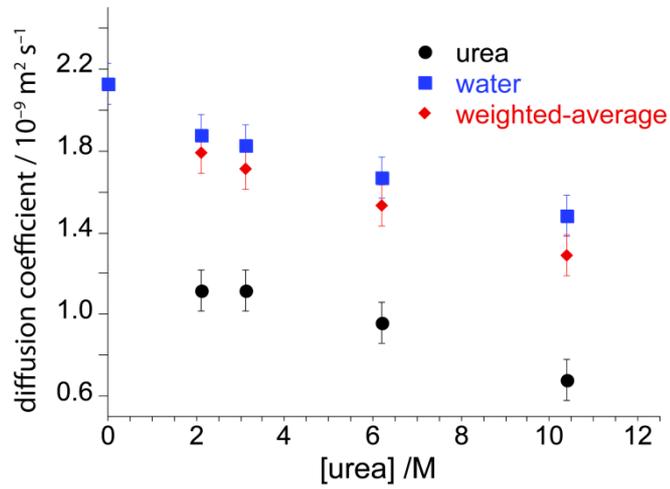
Figure 2. Plot of diffusion coefficients for water and urea, with weighted average of the two, as a function of urea concentration.

Figure 3a shows propagators for a 6.2 M solution of urea in the sponge, at low saturation, at different observation times. The shapes of these propagators are no longer Gaussian, indicating the fluid is confined to a thin layer within the sponge pores. Maximum displacement for P(Z,Δ) increases with increasing Δ, but seems to reach a limit that is probably linked to the spherical geometry of the pore internal surface. By using the infinite planes model (equation 2), it was possible to fit this data (with a fitting error of less than 5 %) and determine D_p. By solving equation 4, the spherical diffusion D_s was determined, which was found to be approximately equal to D_p.
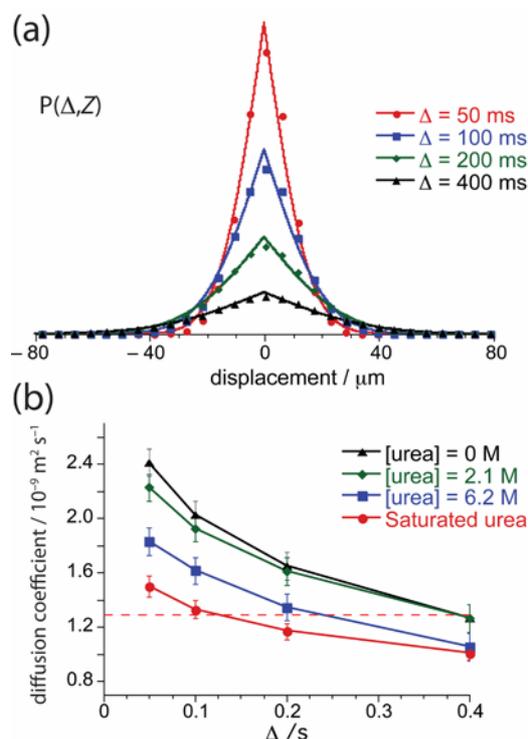
Figure 3. (a) Experimental propagators (dots) at a range of observation times for a urea solution ([urea] = 6.2 M) in sponge. The lines show the fits to the planar diffusion model. (b) Diffusion coefficients (D_s) as a function of Δ for different urea solutions. The red dotted line indicates the weighted-average bulk diffusion coefficient for a saturated urea solution (D = 1.29 $\times$ 10^{-9} m^2 s^{-1})

Figure 4b shows a plot of D_s for different urea concentrations in the sponge at different observation times. As has been observed previously[16], D_s is found to be dependent on the observation time. At short Δ, the infinite plane model breaks down, because the diffusion molecules have not had sufficient time to explore the layer and are diffusing more like molecules in bulk. This leads to the determination of a diffusion coefficient that is too large. At long Δ, the diffusing molecules have sufficient time to diffuse and experience the curvature of the surface of the spherical pore. Hence, again, the infinite plane model is not able to determine the correct diffusion coefficient and instead determines a value for D_s that is too low. In order to identify the optimal observation time for a quantitative diffusion coefficient determination, the values for D_s, for a range of urea solutions, in the sponge are compared with the bulk values of the urea and water weighted diffusion average (Figure 4). These values should be the same, because the composition of the solution in the sponge is controlled and, as there are no significant interactions between the molecules in the solution and the polymeric material of the sponge, the mobility of the molecules should be unaffected by the presence of the sponge. The only differences between the two systems are the shape of the respective propagators and hence the model used to determine the diffusion coefficient. As can be seen from figure 4, it is found that the diffusion coefficients are comparable at Δ = 100 ms. From this observation, and since the prill diameter has similar dimensions to the sponge pores, diffusion coefficients for the prill system are determined at Δ = 100 ms.
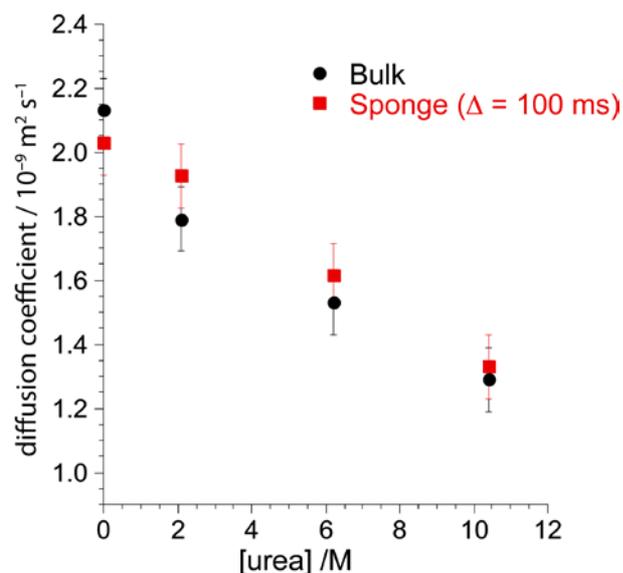
Figure 4. A plot of weighted-average diffusion coefficients for solutions of water and urea in bulk and sponge at Δ = 100 ms

Figure 5a shows propagators for molecules within the prill system at different Δ, with fits to the planar diffusion model (equation 2). It can be seen that the propagators fit well to the planar diffusion model (with a maximum fitting error < 5%) and are similar in shape to those observed for water/urea solutions in the sponge system. This indicates that the liquid in the prill system is predominantly distributed in layers covering the surface of the prills, rather than droplets around the bridges, which would give rise to more Gaussian-like propagators[19]. This observation is consistent with the dye experiments. Using equation 4, D_p values where converted to D_s (with $D_p \sim D_s$). Similarly to the sponge system, the plane model for diffusion has a higher error at Δ = 50 ms and 400 ms. No significant differences were observed between the propagators measured at 1 and 72 hours after set-up.
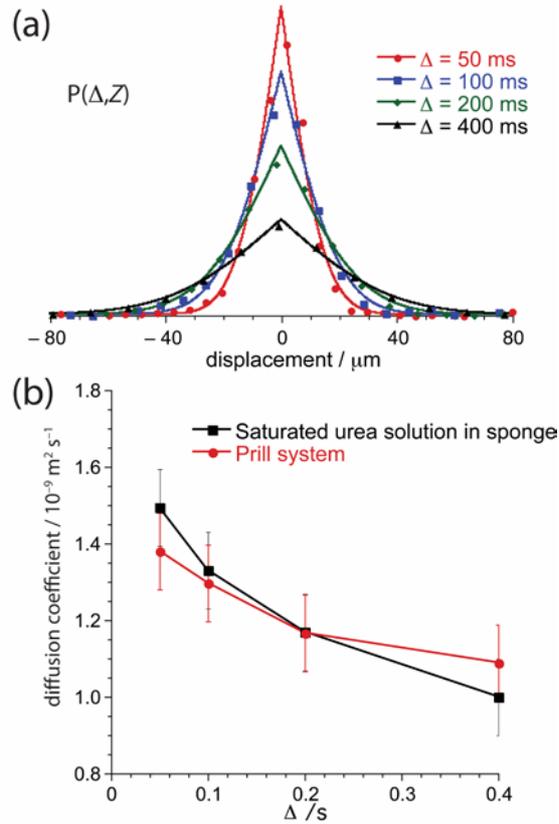
Figure 5.(a) Experimental propagators (dots) at different observation times Δ during urea prill caking, 1 hour after set-up, with fits (lines) to the planar diffusion model.(b) A plot of diffusion (D_s) against Δ for prill and sponge systems.

The plot in Figure 5b allows comparison between values of D_s in the prill system with those of the saturated solution in the sponge, as a function of Δ. There is good agreement at $\Delta = 100$ - 200 ms. However, at $\Delta = 50$ ms, a lower value is observed for diffusion in the prill system, possibly reflecting that there are some smaller pores in the sponge compared to the sizes of the urea prills. At $\Delta = 100$ ms, a value of D_s, = 1.35×10^{-9} m^2 s^{-1} is observed for the prill system. This value is close to D_s determined for saturated urea solutions in both the bulk and sponge, indicating the layer on the surface of the prill is composed of a saturated urea solution. Hence, these results not only provide quantitative details about the mobility of molecules in liquids films on the prill surface, they also inform us of their composition. These data could also provide an estimate of the thickness of the layer. As the limit for application of the infinite plane model is around $\Delta = 50$ ms, it suggests that mean displacement ($\sqrt{2D\Delta}$) of molecules in the layer, over this time, is comparable to the thickness of the layer. Using a value of $D_s = 1.35 \times 10^{-9}$ m^2 s^{-1}, the mean displacement is determined to be 12 μm at $\Delta = 50$ ms, suggesting that the layer thickness is of the order of 10^{-5} m.

Conclusions

In this paper, we have applied NMR diffusion measurements to probe the composition, distribution and molecular mobility of water either within a sponge at low-water saturation or absorbed onto the surface of urea prills during caking. In both systems, the resulting propagators show a non-Gaussian shape, indicating the fluid is distributed as thin films on the surfaces of the urea prills or pore walls in the sponge. To these data, we applied the infinite planes model proposed by Holmes et al.[16] and have been able to provide the first quantitative measurements of diffusion on spherical sponge pores and prills. Our measurements have confirmed that in the urea prill system, the absorbed water is uniformly located on the surface of the caking prills; that urea dissolves into this absorbed water, forming a saturated urea solution, and that the molecular diffusion coefficients in this film are the same as those found in bulk solution. Through analysis of the data, as a function of observation time, it was possible to estimate that the thickness of the liquid layer was on the order of 10^{-5} m. We believe these types of measurements not only represent an excellent method for developing and testing strategies for minimizing caking in hygroscopic particle systems, but also offer unique insight into the formation and characterisation of thin liquid layers formed within a range of environments and applications, particularly where samples are opaque and cannot be studied using optical methods. .

References

(1) Billings, S. W.; Bronlund, J. E.; Paterson, A. H. J. Effects of capillary condensation on the caking of bulk sucrose. *J. Food Eng.* **2006,** *77*, (4), 887-895.
(2) Langlet, M.; Benali, M.; Pezron, I.; Saleh, K.; Guigon, P.; Metlas-Komunjer, L. Caking of sodium chloride: Role of ambient relative humidity in dissolution and recrystallization process. *Chem. Eng. Sci.* **2013,** *86*, 78-86.
(3) Rutland, D. W. Fertilizer Caking - Mechanisms, Influential Factors, and Methods of Prevention. *Fert. Res.* **1991,** *30*, (1), 99-114.
(4) Nie, X. D.; Evitts, R. W.; Besant, R. W. Simulation of Moisture Uptake and Transport in a Bed of Urea Particles. *Ind. Eng. Chem. Res.* **2008,** *47*, (20), 7888-7896.
(5) Walker, G. M.; Magee, R. A.; Holland, C. R.; Ahmad, M. N.; Fox, J. N.; Moffatt, N. A.; Kells, A. G. Caking processes in granular NPK fertilizer. *Ind. Eng. Chem. Res.* **1998,** *37*, (2), 435-438.
(6) Brockel, U.; Wahl, M.; Kirsch, R.; Feise, H. J. Formation and growth of crystal bridges in bulk solids. *Chem. Eng. Technol.* **2006,** *29*, (6), 691-695.
(7) Peng, S. W.; Strathdee, G.; Besant, R. W. Dissolution reaction of potash fertilizer with moisture. *Can. J. Chem. Eng.* **1999,** *77*, (6), 1127-1134.
(8) Wang, Y.; Evitts, R. W.; Besant, R. W. Modelling crystal growth between potash particles near contact points during drying processes. Part I: Problem formulation. *Can. J. Chem. Eng.* **2008,** *86*, (2), 192-198.
(9) Tanaka, T. Evaluating caking strengths of powders. *Ind. Eng. Chem. Prod. RD* **1978,** *17*, (3), 241-246.
(10) de Meer, S.; Spiers, C. J.; Nakashima, S. Structure and diffusive properties of fluid-filled grain boundaries: An in-situ study using infrared (micro) spectroscopy. *Earth Planet. Sci. Lett.* **2005,** *232*, (3-4), 403-414.

(11) Koelemeijer, P. J.; Peach, C. J.; Spiers, C. J. Surface diffusivity of cleaved NaCl crystals as a function of humidity: Impedance spectroscopy measurements and implications for crack healing in rock salt. *J. Geophys. Res.: Solid Earth* **2012,** *117*.

(12) Wahl, M.; Kirsch, R.; Brockel, U.; Trapp, S.; Bottlinger, M. Caking of urea prills. *Chem. Eng. Technol.* **2006,** *29*, (6), 674-678.

(13) Kirsch, R. M.; Williams, R. A.; Brockel, U.; Hammond, R. B.; Jia, X. D. Direct Observation of the Dynamics of Bridge Formation between Urea Prills. *Ind. Eng. Chem. Res.* **2011,** *50*, (20), 11728-11733.

(14) Callaghan, P. T. *Translational dynamics and magnetic resonance : principles of pulsed gradient spin echo NMR*. Oxford University Press: Oxford ; New York, 2011.

(15) Callaghan, P. T.; Macgowan, D.; Packer, K. J.; Zelaya, F. O. High-Resolution Q-Space Imaging in Porous Structures. *J. Magn. Reson.* **1990,** *90*, (1), 177-182.

(16) Holmes, W. M.; Graham, R. G.; Packer, K. J. Diffusion in surface-wetting films in a two-phase saturated porous solid characterised by pulsed magnetic field gradient NMR. *Chem. Eng. J.* **2001,** *83*, (1), 33-38.

(17) Stejskal, E. O.; Tanner, J. E. Spin Diffusion Measurements: Spin Echoes in the Presence of a Time-Dependent Field Gradient. *J. Chem. Phys.* **1965,** *42*, (1), 288-292.

(18) Packer, K. J.; Stapf, S.; Tessier, J. J.; Damion, R. A. The characterisation of fluid transport in porous solids by means of pulsed magnetic field gradient NMR. *Magn. Reson. Imaging* **1998,** *16*, (5-6), 463-469.

(19) Holmes, W. M.; Packer, K. J. Investigation of thin surface-wetting films in two-phase saturated porous media. *Magn. Reson. Chem.* **2002,** *40*, S20-S28.

(20) Wexler, A.; Hasegawa, S. Relative Humidity-Temperature Relationships of Some Saturated Salt Solutions in the Temperature Range 0-Degree to 50-Degrees-C. *J. Res. Natl. Bur. Stand. (U. S.)* **1954,** *53*, (1), 19-26.

(21) Sorell, L. S.; Myerson, A. S. Diffusivity of Urea in Concentrated, Saturated and Supersaturated Solutions. *Aiche J.* **1982,** *28*, (5), 772-779.