Observation and analysis of the infiltration of polymer liquids into carbon black agglomerates

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(Received 18 February 1997; accepted 21 July 1997)

Abstract—The infiltration of polymeric liquids into carbon black agglomerates has been studied using buoyancy measurements. Both the rate of infiltration and the degree of saturation decrease with increasing matrix viscosity. The influence of interfacial chemistry was demonstrated by comparing the enhanced infiltration and saturation that occurs with polybutadiene and ethylene propylene copolymers in comparison to polydimethyl siloxane liquids. However, the differences attributable to interfacial chemistry are masked when highly viscous liquids are used. The influence of the agglomerate pore structure on infiltration and saturation characteristics was also examined. In the case of low-structure carbon black, the infiltration and saturation characteristics showed a sensitivity to packing density while the same was not true for agglomerates of the high structure carbon black. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Infiltration; saturation; agglomerate structure.

INTRODUCTION

Carbon black is one of the most important fillers for the rubber and polymer industries. The success of dispersive mixing operations applied to carbon black agglomerates depends in part on the cohesivity of the powder agglomerates. The nature and strength of the cohesive forces within the agglomerate can be affected by the presence of moisture (Schubert et al., 1975) or other fluids such as low viscosity polymers (Horwatt et al., 1989). When agglomerates are introduced into polymers, favorable interfacial interactions will result in the wetting and spreading of the matrix fluid on the surface of the solids comprising the agglomerates and infiltration of the matrix within the interior of the agglomerate. These processes may change agglomerate cohesive forces over the course of processing.

In order to understand this infiltration process, one must consider the interfacial forces which drive the infiltration, the viscous nature of the matrix fluids which acts to retard the infiltration, and the geometry of the pore space within the agglomerates. The structure of carbon black can be described on the length scale of the agglomerate or on the length scale of the aggregates which comprise the agglomerate. The morphology of aggregates is usually specified in terms of the structure or grade of carbon black. The packing density or arrangement of these aggregates within the agglomerates determines the overall agglomerate density. The void space within agglomerates can be classified into two types; those voids within an aggregate, and the voids between aggregates (Medalia, 1970).

Due to the complex geometry of the voids within agglomerates, the process of liquid infiltration is expected to result in a complicated distribution of liquid and entrapped air within the agglomerate. The hydrodynamic friction resisting infiltration and the capillary forces that drive infiltration depend differently on the shape and size of the pores within the porous agglomerate. Larger pores offer less resistance to flow, but the capillary forces driving the infiltration will be larger in the small diameter pores for liquids that interact well with the solid. We envision that the bulk of liquid infiltration occurs through the larger diameter pores. During this process, much of the air initially present within the agglomerate will be vented through similar large-diameter preferred pathways. Subsequently, capillary forces will tend to drive the filling of smaller sized voids that were initially bypassed during the infiltration through the large pores. However, these small voids may act as closed pores, and the associated residual air may be entrapped by
the infiltrating liquid. This entrapped air will be compressed by the capillary forces until it reaches a pressure that counterbalances the surface tension forces, at which time a mechanical equilibrium is attained. Thus, we expect that the final state can be characterized by a less than complete saturation of the voids by the infiltrating liquid. For the case of fluids having low viscosity and high affinity for the solids, the filling of the small voids can occur quite readily and simultaneously with the filling of the large voids. In this case, degrees of saturation near 100% may be expected. In any event, the presence of any liquid–gas interfaces within agglomerates and the associated surface tension forces can contribute significantly to the overall cohesivity of the agglomerate.

The goal of this paper is to measure and model liquid infiltration into spherical carbon black agglomerates, and to examine the influence of system parameters on the infiltration. Specifically, the dependence of the infiltration kinetics and the degree of saturation within the carbon black agglomerates on viscosity, types of liquid, agglomerate density and aggregate structure were investigated. The measurement technique and the model for the results were based on those reported by Bohin et al. (1994, 1995).

**EXPERIMENTAL**

**Materials**

Two types of fluffy carbon black, Monarch®900* and Monarch®880* provided by Cabot Corporation, were used in this study. Some morphological characteristics of the two grades are listed in Table 1. Both grades have the same primary particle size, as reflected by the BET surface area, but they possess different aggregate structure; Monarch®880 is designated as a high structure black whereas Monarch®900 is a low structure grade.

Spherical agglomerates were made by unidirectionally compressing and tumbling the fluffy carbon black aggregates into 2.2–2.3 mm diameter spheres. The agglomerates were prepared with densities ranging from 0.30 to 0.38 g/cm³ as measured by pycnometry with a very high viscosity fluid (600,000 cS polydimethylsiloxane) for which no infiltration of the pores was expected during the measurement period.

The polymeric fluids used in this work are polydimethyl siloxane (PDMS) of five different viscosities (3400, 4700, 16,400, 48,000 and 60,000 cS), polybutadiene (PBD) fluids of 3400 and 48,000 cS, ethylene–propylene copolymer (EP) of 4700 cS, and styrene–polybutadiene copolymer (SB) (30% styrene) of 16,400 cS. All PDMS fluids were supplied by the Dow Corning Corporation. The PBD and SB fluids used were supplied by Ricon Resins, Inc. while the EP was supplied by Uniroyal Chemical Company, Inc. Table 2 shows some important characteristics for the test liquids.

**Procedures**

*Matrix infiltration.* The kinetics of matrix infiltration was measured in buoyancy experiments performed with initially dry agglomerates. A schematic diagram of the experimental setup for the sedimentation is shown in Fig. 1. The flotation or settling velocity of the various agglomerates was recorded as a function of the time of immersion in the different polymers using a CCD camera and an image analysis systems as detailed elsewhere (Bohin et al., 1995).

*Contact angle measurement.* The various test fluids are expected to interact differently with carbon black. The relative strength of this interactions can be gauged by measuring contact angles. Figure 2 shows a schematic based on a standard method (Heertjes and Kossen, 1967; Wu and Brzozowski, 1971) in which the shape of droplets of the test liquids on

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*Table 1. Some morphological characteristics of the carbon black aggregates.*

<table>
<thead>
<tr>
<th>Grade</th>
<th>BET Surface Area (m²/g)</th>
<th>Dibutyl Phthalate Absorption(cm³/100 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monarch®900</td>
<td>205</td>
<td>70</td>
</tr>
<tr>
<td>Monarch®880</td>
<td>205</td>
<td>112</td>
</tr>
</tbody>
</table>

*Table 2. Density and surface tension of the liquid polymers used.*

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Density (g/cm³)</th>
<th>γLV (mJ/m²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS</td>
<td>0.97</td>
<td>21.3</td>
<td>Mark (1985)</td>
</tr>
<tr>
<td>PBD</td>
<td>0.89</td>
<td>32.5</td>
<td>van Krevelen (1990)</td>
</tr>
<tr>
<td>EP</td>
<td>0.84</td>
<td>32.1</td>
<td>van Krevelen (1990)</td>
</tr>
<tr>
<td>SB</td>
<td>0.90</td>
<td>35.7</td>
<td>van Krevelen (1990)</td>
</tr>
</tbody>
</table>

*Monarch® is a registered trademark of Cabot Corporation.
Fig. 1. Schematic diagram of the buoyancy experiment.

Fig. 2. Schematic diagram of contact angle measurement.

For a powder compact, the apparent contact angle is different from the true contact angle due to the influence of microscale surface roughness (Wu, 1982). Heertjes and Kossen (1967) took into account the effect of the roughness of a powder compact and proposed that the contact angle can be deduced from the drop height, for contact angles ranging from $0^\circ$ to $90^\circ$, according to

$$\cos \theta = 1 - \left( 3(1 - \varepsilon) \left( \frac{2 \gamma_{LV}}{\rho_l g h^2} - \frac{1}{2} \right) \right)^{1/2}. \quad (1)$$

Here, $\varepsilon$ is the porosity of the powder compact, $h$ is the maximum height of the drop, $g$ is the acceleration of the gravity, $\rho_l$ is the density of the liquid, and $\gamma_{LV}$ is the surface tension of the liquid.

**MODELING STUDIES**

**Kinetics of matrix infiltration**

A schematic diagram for a spherical agglomerate undergoing matrix infiltration is shown in Fig. 3. Here, $a$ is the agglomerate radius and $R$ is the radius of interior part of the agglomerate that has not yet been infiltrated. Taking Darcy’s law (Greenkorn, 1983) to be valid for the flow of the matrix within the agglomerate, it can be shown that the kinetics of infiltration are described by

$$\frac{d^2}{6} \left( 2 \left( \frac{R}{a} \right)^3 - 3 \left( \frac{R}{a} \right)^2 + 1 \right) = \frac{k_w}{\mu} P_c t \quad (2)$$

where $\mu$ is the matrix viscosity, $k_w$ is the permeability of the agglomerate to the liquid, $P_c$ is the capillary pressure in the liquid at position $r = R$, and $t$ is the immersion time. A detailed derivation of this relationship and a description of the restrictions involved in its use are provided in the Appendix.

**Effective permeability**

The effective permeability within a porous medium depends on the degree of fluid saturation, $S$. Empirical results (Allen et al., 1988) show that

$$k_w = k_{sat} S^n \quad (3)$$

where $k_{sat}$ is the intrinsic permeability or permeability at full saturation of the porous medium and $S$ is the degree of saturation. The exponent, $n$, usually ranges between 3 and 4 (Corey, 1954; Lipinski, 1980; Topp and Miller, 1966; Bear, 1972); for a porous media consisting of monodisperse spheres, $n = 3$ (Topp and Miller, 1966; Bear, 1972). The correlation expressed by eq. (3) formally applies to the case in which $S$ is invariant in time. In our conceptual model of the filling of voids within agglomerates, the saturation at a particular location will have some dynamic character and $S$ will increase with time as more of the smaller voids become filled. As a first approximation for the purposes of modeling the permeability within agglomerates being infiltrated, we take $S$ to be the ultimate degree of saturation that is achieved by the infiltrating liquid.

**Capillary pressure**

The capillary pressure in a partially saturated porous medium depends on the size of the pores yet to be filled by the infiltrating medium. While there have been studies (Topp and Miller, 1966; Reed et al., 1987; Scheidegger, 1957; Rose and Bruce, 1949) of the relationship between the equilibrium capillary pressure and saturation level, to our knowledge there has never been a study of the capillary pressure as a function of saturation for the case of ongoing liquid infiltration. For a wetting liquid, the equilibrium case corresponds to one in which all pores smaller than a critical size are filled by the liquid. This is different than in our
case of ongoing infiltration, in which most of the larger pores are expected to be filled, and the smaller pores may be blocked from filling by entrapped air. Furthermore, the distribution of filled and unfilled pores is expected to be a function of position within the infiltrated region, with a larger fraction of pores filled near \( r = a \) than near \( r = R \).

Following the lead of Levertt (1941), we propose that the capillary pressure within an agglomerate being infiltrated can be represented by

\[
P_i = \frac{\gamma_{LV} \cos \theta}{\sqrt{k_{sat}/\varepsilon}} Y(S). \tag{4}
\]

Here, the term \( \sqrt{k_{sat}/\varepsilon} \) can be interpreted as a mean pore diameter for the porous medium. The term \( Y(S) \) embodies distribution of filled and unfilled voids within the agglomerate and thus should depend on the degree of saturation within the infiltrated layer, \( R < r < a \). Based on the results from the equilibrium studies \( Y(S) \) will not depend very strongly on \( S \), except for very low saturation levels, and low saturation levels are not expected in the present situation, except perhaps at the initial stages of infiltration.

**Estimation of infiltration volume and depth of infiltration**

Assuming that fluid infiltration occurs in a spherically symmetric fashion as depicted in Fig. 3, the extent of the non-infiltrated interior region can be calculated from simple geometric considerations as

\[
X = \frac{R}{a} = (1 - \frac{3V_i}{4\pi a^2 S})^{1/3} \tag{5}
\]

where \( V_i \) is the total volume of matrix fluid that has been incorporated into the agglomerate. Combination of eqs (2)-(4) and the definition in eq. (5) yields

\[
2X^3 - 3X^2 + 1 = Ct \tag{6}
\]

where

\[
C = \frac{6\sqrt{k_{sat}/\gamma_{LV} \cos \theta}}{a^2 \mu} S^3 Y(S). \tag{7}
\]

Equations (5)-(7) relate the infiltration volume \( V_i \) and size of the non-infiltrated region \( X \) to immersion time. For similar porous media \( k_{sat} \) and \( \varepsilon \) are fixed values and the value of \( \gamma_{LV} \cos \theta/\mu \) will depend only on the matrix fluid.

In order to access \( V_i(t) \), we measured the variation of flotation rates of initially dry agglomerates with time of immersion. For an agglomerate moving at speed \( U \) through a stagnant fluid, a force balance on the agglomerate gives

\[
\frac{4}{3} \pi a^3 g (\rho_b - \rho_f) = 6\pi \mu a U \Omega \tag{8}
\]

where \( \rho_b \) is the net density of the agglomerate and any incorporated fluid and \( \rho_f \) is the density of the fluid. The parameter \( \Omega \) is the ratio of the hydrodynamic drag for a permeable sphere to that of an impermeable sphere of equivalent density and size. The value of \( \rho_b \) can be expressed in terms of the total volume of matrix fluid incorporated within the agglomerate, \( V_i \), as

\[
\rho_b = (1 - \varepsilon)\rho_s + \frac{V_i}{\frac{4}{3}\pi a^3} \rho_f \tag{9}
\]

where \( \rho_s \) is the density of solid carbon black (1.86 g/cm\(^3\)). Combining eqs (8) and (9) yields

\[
V_i = \frac{4}{3} \pi a^3 \left\{ \frac{9\mu U}{2ga^2 \rho_f} + 1 - \frac{(1 - \varepsilon)\rho_s}{\rho_f} \right\}. \tag{10}
\]

Thus, values of \( V_i \) can be estimated by measuring the sedimentation or flotation velocity of the agglomerate, \( U \). The value of \( \Omega \) is expected to depend on the degree of fluid saturation within the agglomerate. However, infiltration of the periphery of the agglomerate occurs very quickly, (Yamada et al., 1970). Thus, as an approximation, the saturation level of the periphery is taken to be equivalent to that for an agglomerate soaked for extended periods of time.

**EXPERIMENTAL RESULTS AND DISCUSSION**

**Contact angle**

Table 3 shows the results of contact angle measurements for the four liquid polymers on carbon black compacts. Contact angles alone cannot be used for the comparison of the wetting characteristics of the different liquids. Instead, the product of the surface tension and the cosine of the contact angle is used as a gauge of the relative strength of the interfacial interaction between the various liquids and carbon black (Patton, 1970). These values are also presented in Table 3. Since PBD, EP and SB show higher \( \gamma_{LV} \cos \theta \) values than PDMS due to their higher surface tension, these fluids may be expected to exhibit enhanced infiltration kinetics or higher saturation values within carbon black agglomerates.

Note that Young's equation, which characterizes the wetting of liquids on ideal (flat, smooth and homogeneous) surfaces, would predict that \( \gamma_{LV} \cos \theta \) would be a constant for a given solid. The variation exhibited by the results in Table 3 can be attributed to nonidealities, especially less than complete saturation of the pores of the carbon black compacts.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( \cos \theta )</th>
<th>( \gamma_{LV} \cos \theta ) (mJ/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS</td>
<td>0.98</td>
<td>20.9</td>
</tr>
<tr>
<td>PBD</td>
<td>0.98</td>
<td>31.9</td>
</tr>
<tr>
<td>EP</td>
<td>0.99</td>
<td>31.8</td>
</tr>
<tr>
<td>SB</td>
<td>0.99</td>
<td>35.3</td>
</tr>
</tbody>
</table>
**Liquid infiltration kinetics**

The experimentally determined values of $V_i$ calculated from the buoyancy measurements [eq. (7)] for agglomerates comprised of the two grades of carbon black and PDMS fluids of viscosity 3400, 4700 and 16,400 cS are shown in Figs 4, 5 and 6, respectively. Due to the times involved in starting up an experiment, the first data obtained from a buoyancy experiment can be taken no earlier than 10 min after the agglomerate first contacts the test fluid. The increase in $V_i$ with immersion time signals the ongoing liquid infiltration.

For each of the PDMS fluids, the magnitude of $V_i$ decreases with an increase in the agglomerate density. This results from the reduced interior void volume at higher agglomerate packing density. At comparable overall packing density, the low structure black showed an overall higher value of $V_i$ than the high structure black which can be attributed to the difference in the pore size distributions in the two cases. As the matrix viscosity increases, values of $V_i$ decrease for each agglomerate density and both grades of carbon black.

Infiltration kinetics for agglomerates of the two grades of carbon black for the 3400 cS PBD, the 4700 cS EP, and the 16,400 cS SB are shown in Figs 7, 8 and 9, respectively. Since the infiltration is strongly influenced by matrix viscosity, $V_i$ values for each of the above polymers should only be compared directly with the infiltration results for PDMS of comparable viscosity. In the case of PBD, the $V_i$ values are higher than that of PDMS for the whole range of agglomerate densities for the low structure carbon black, but remain almost unchanged for the high structure material (see Figs 4 and 7). There is no clear difference in the infiltration kinetics between EP and PDMS, or SB.
Fig. 6. Infiltrated volume as a function of immersion time for PDMS (16,400 cS) into carbon black agglomerates: (a) low structure black; (b) high structure black.

Fig. 7. Infiltrated volume as a function of immersion time for PBD (3400 cS) into carbon black agglomerates: (a) low structure black; (b) high structure black.

Fig. 8. Infiltrated volume as a function of immersion time for EP (4700 cS) into carbon black agglomerates: (a) low structure black; (b) high structure black.
Fig. 9. Infiltrated volume as a function of immersion time for SB (16400 cS) into carbon black agglomerates: (a) low structure black; (b) high structure black.

Table 4. Summary of pore size distributions in agglomerates

<table>
<thead>
<tr>
<th>Grade</th>
<th>Monarch® 900</th>
<th>Monarch® 880</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agglomerate density (g/cm³)</td>
<td>0.381</td>
<td>0.378</td>
</tr>
<tr>
<td>Total intrusion volume (cm³/g)</td>
<td>1.681</td>
<td>1.637</td>
</tr>
<tr>
<td>Pores within aggregates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range of pore sizes (nm)</td>
<td>3–18.9</td>
<td>3–19.5</td>
</tr>
<tr>
<td>Peak pore diameter (nm)</td>
<td>9.2</td>
<td>13.0</td>
</tr>
<tr>
<td>Intrusion volume (cm³/g)</td>
<td>0.439</td>
<td>0.560</td>
</tr>
<tr>
<td>Pores between aggregates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range of pore sizes (nm)</td>
<td>19.5–7229</td>
<td>20.1–7229</td>
</tr>
<tr>
<td>Peak pore diameter (nm)</td>
<td>1590</td>
<td>825</td>
</tr>
<tr>
<td>Intrusion volume (cm³/g)</td>
<td>1.242</td>
<td>1.077</td>
</tr>
</tbody>
</table>

and PDMS of comparable viscosity (cf. Figs 5 and 8, or 6 and 9, respectively).

Effect of agglomerate structure on infiltration characteristics

The two grades of carbon black exhibited different behavior in the infiltration and saturation levels even if the same overall density of the agglomerate was used. Aggregates of different morphologies will pack differently within agglomerates resulting in different internal void distributions. For carbon black agglomerates, the voids fraction within an agglomerate, εi, can be classified in two different categories; voids within aggregates and those between aggregates:

\[ \varepsilon = \varepsilon_i + \varepsilon_o. \]  
(11)
Here, \( \varepsilon_i \) is the ratio of the volume of the pores within aggregates to the overall agglomerate volume, and \( \varepsilon_o \) is the ratio of the volume of the pores between aggregates to the overall agglomerate volume.

Pore size distributions were obtained from mercury porosimetry results (reported by Micromeritics Analytical Laboratories, Norcross GA). Table 4 summarizes these results for agglomerates of both grades. The pore size within the aggregates were found to be narrowly distributed around 9.2 nm for the low structure carbon black and 13 nm for the high structure black. On the other hand, the size of the pores between aggregates, which depends on the packing density of the agglomerates, shows very broad distributions in the range from nanometer to micron scale.

The ratio of the pores between aggregates to the total pores within agglomerates, \( \varepsilon_o/\varepsilon \), can be estimated from the intrusion volume measured by mercury porosimetry:

\[ \varepsilon_o/\varepsilon = (\text{The intrusion volume between aggregates})/(\text{Total intrusion volume}). \]
Table 5 shows the \( \varepsilon_o/\varepsilon \) values for agglomerates of both grades from the mercury porosimetry data. The low
structure black, Monarch® 900 shows higher $e_o/e$ values than the high structure black at the same agglomerate density, which may cause the higher infiltration and saturation levels for the low structure black.

All the fluids studied here show higher $V_i$ values for the low structure grade at comparable soaking times and for agglomerates of similar density. This may suggest that the largest pores between the aggregates within the agglomerate are preferred pathways for fluid infiltration. Assuming that the degree of fluid saturation within the infiltrated region is related to the fraction of pores between the aggregates (i.e. $S = e_o/e$), one can calculate the relative size of the uninfiltred core from eq. (5).

Figures 10 and 11 show plots of the left-hand side of eq. (6) as a function of immersion time for agglomerates of similar density but different grades. These results were obtained from the data shown in Figs 4–9 using eq. (5) to translate the $V_i$ data into values of $X$. It is interesting to note that each set of results can be well correlated by a straight line, which supports the validity of the infiltration model. Note however that eq. (6) predicts that these data should have a zero intercept at zero immersion time. The offset in the data can be attributed to two factors. First, the value of $\Omega$ used in computing the measured flotation rates into $V_i$ is only an approximation to the actual friction coefficient during the initial stages of infiltration. Secondly, the value of $Y(S)$ used in eq. (7) may be different in the initial stages of infiltration compared to later times.

Figure 12 shows the dependence of $C$ on the matrix properties for both grades of carbon black. It is interesting to note that $C$ values increase almost linearly with $\gamma \cos \theta / \mu$ and there are no striking differences between the two grades of carbon black. This indicates $\sqrt{k_{sat}e}$ is approximately the same for agglomerates of similar density regardless of the grade of aggregate from which they are prepared. The only exception to this trend is for the 3400 cS PBD in the experiments performed with Monarch® 900. This deviation can be attributed to a different saturation level attained with this fluid.

**CONCLUSIONS**

For various combinations of liquid polymers and carbon black agglomerates, the infiltration kinetics has been studied using a buoyancy technique. At comparable agglomerate densities, the volume of fluid incorporated, $V_i$, was found to decrease with an increase in the viscosity of PDMS. Values of $V_i$ for 3400
Infiltration of polymer liquids into carbon black agglomerates

Infiltration kinetics as a function of immersion time for various fluids in agglomerates of the high structure carbon black (density $0.344 \text{ g/cm}^3$).

Fig. 12. Plots of the parameter $C$ as a function of the fluid parameter $\gamma_{lv} \cos \theta / \mu$ for both the low (density $0.347 \text{ g/cm}^3$) and high structure carbon black (density $0.344 \text{ g/cm}^3$). For each fluid type, larger symbols are used to denote the result for the high structure black while smaller symbols indicate the results for the low structure carbon black.

The infiltration rates for the high structure grade might be due to the higher $\epsilon_d$ values at the same agglomerate density.

The measured infiltration kinetics were well correlated by our infiltration model, which separately accounts for fluid properties and structural characteristics of the agglomerates.

Acknowledgment

The authors are grateful to Bridgestone Corporation for their fellowship support (HY). The authors also acknowledge the financial support of Cabot Corporation.

REFERENCES


**APPENDIX: DEVELOPMENT OF THE KINETIC MODEL FOR MATRIX INFILTRATION**

As is depicted in the schematic diagram shown in Figure 3, we assume that the infiltration proceeds in a manner that retains spherical symmetry. According to Darcy’s law, the speed of motion of a fluid within a porous medium, \( v_w \), is given by

\[
    v_w = -k_w \frac{dP}{\mu} \frac{1}{dr}. \tag{A1}
\]

where \( k_w \) is the effective permeability of the porous medium and \( dP/dr \) is the pressure gradient driving the flow. The volumetric flow rate of the infiltrating fluid, \( q_w \), can be expressed as

\[
    q_w = -4\pi r^2 v_w. \tag{A2}
\]

Since the fluid is assumed to be incompressible, \( q_w \) is a constant in the region \( R < r < a \), and eqs (A1) and (A2) can be integrated over \( r \) to yield

\[
    P_{l,R} - P_{l,a} = \frac{q_w \mu}{4\pi k_w} \left( \frac{1}{a} - \frac{1}{R} \right) \tag{A3}
\]

where \( P_{l,R} \) is the liquid-phase pressure at \( r = R \) and \( P_{l,a} \) is the liquid-phase pressure on the exterior of the agglomerate, \( r = a \).

In a buoyancy experiment, the agglomerate will sample different elevations within the fluid during the course of an experiment. For an agglomerate located at position \( H \) from the upper surface of the fluid, the pressure in the fluid on the exterior of the agglomerate is

\[
    P_{l,a} = \rho g H + P_{sim} \tag{A4}
\]

where \( P_{sim} \) is the atmospheric pressure. Also, the capillary pressure at the liquid–gas interface, \( P_c \), can be expressed as

\[
    P_c = P_{a,R} - P_{l,R} \tag{A5}
\]

where \( P_{a,R} \) is the pressure in the gas phase at position \( r = R \). Since most of the air initially present within the agglomerate is vented from the agglomerate \((P_{a,R} \approx P_{sim})\), then

\[
    P_{l,a} - P_{l,R} = \rho g H + P_{sim} + P_c - P_{a,R} = \rho g H + P_c \tag{A6}
\]

Since the capillary pressure is inversely proportional to the hydrodynamic radius of the capillary and the pore radius is very small (\( \sim 0.5 \mu m \)), the term \( \rho g H \) can be neglected compared to the capillary pressure term since \( H \) is small (\( \sim 50 \) mm) in the buoyancy experiments.

With this approximation, eq. (A3) becomes

\[
    P_r = -\frac{q_w \mu}{4\pi k_w} \left( \frac{1}{a} - \frac{1}{R} \right) \tag{A7}
\]

in which \( P_r \) should be a constant for a given fluid, in a given porous medium, at a fixed saturation value. The volumetric flow rate can also be expressed in terms of the advance of the liquid–solid interface

\[
    q_w = -4\pi R^2 \frac{dR}{dr}. \tag{A8}
\]

Substituting eq. (A7) into eq. (A8) and integrating over time yields eq. (2).