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Upward Infiltration into Porous Media as Affected by Wettability and Anionic Surfactants

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ABSTRACT

The influence of surfactants on water infiltration has not been thoroughly evaluated due to the diversity and complexity of soils. The purpose of this study was to propose an equation for upward infiltration by capillary action under gravity based on Darcy's law and to use the equation to determine the effect of an anionic surfactant on infiltration in porous materials. We showed that this new equation is equivalent to the Washburn equation, which has been widely used for measuring contact angles in powdered solids. We examined upward infiltration of sodium dodecyl sulfate (SDS; from 0 to 700 mol m⁻³) into dry materials. The new equation evaluated infiltration well. In glass beads and sand, which are both hydrophilic, the infiltration rate decreased as the SDS concentration increased due to a decrease in solution surface tension (from 72 to 38 mN m⁻¹). Major changes in the contact angle were not observed. In polyethylene particles and peat moss, which are hydrophobic organic materials, the infiltration rate increased as the SDS concentration increased, mainly because of the decrease in the contact angle (from >125° to 69° for polyethylene, from 102° to 43° for peat moss). In leaf mold, the infiltration rate decreased as the SDS concentration increased due to the decrease in the saturated hydraulic conductivity caused by swelling. SDS adsorption probably resulted in swelling. Surface tension, contact angle, and adsorption, which were all affected by SDS concentration, caused the different infiltration rates.

Abbreviations: SDS, sodium dodecyl sulfate; CMC, critical micelle concentration.

22 Surfactants are used in detergents, shampoos, and chemical fertilizers as an anti-caking agent, in
23 agricultural chemicals as an emulsifying agent, and for other uses. Surfactants are also used for
24 remediating contaminated soil, enhancing oil recovery (West and Harwell, 1992), and ameliorating
25 soil-water repellency (Cisar et al., 2000; Kostka, 2000). Enormous quantities have been used, and much
26 waste material has been discharged into the environment (Lewis, 1991). Because surfactants degenerate
27 cells (Sakashita, 1979), they strongly affect living organisms and ecosystems (Lewis, 1991). Their overall
28 influence on the soil environment is not fully understood.

29 Solid surface characteristics are changed when surfactants are adsorbed on solid surfaces (Koopal et
30 al., 1999). Surfactants also decrease water surface tension. Therefore, surfactants influence water and
31 solute movement in soils. The influence of surfactant concentration on unsaturated flow caused by the
32 depression of surface tension has been reported (Karkare and Fort, 1994; Smith and Gillham, 1994, 1999;
33 Henry et al., 1999; Henry and Smith, 2002). Surfactant application increases the infiltration rate into
34 hydrophobic soils consisting of sands coated with organic compounds (Pelishek et al., 1962; Feng et al.,
35 2002). The application of nonionic surfactant either before or with irrigation increases the dispersion of a
36 hydrophobic sandy loam (Mustafa and Letey, 1969), and this dispersion decreases flow rates in the soil
37 (Miller et al., 1975). Soil hydraulic conductivity decreases when sodium dodecyl sulfate (SDS) is applied
38 due to precipitation of the divalent electrolyte dodecylsulfate (Liu and Roy, 1995). Both nonionic and
39 ionic surfactants affect hydraulic conductivity reduction in loam and sand (Allred and Brown, 1994). Most
40 organic compounds are surface-active in aqueous solution and can reduce water surface tension (Henry
41 and Smith, 2002), and may change the contact angle of a porous material. Surfactants are used for
42 remediation of the vadose zone or unconfined aquifers. Therefore, considering the effects of surfactants on
43 water flow is important, and these effects must be evaluated by a proper water flow equation.

44 Because the liquid-solid contact angle is an index of soil wettability, it has been measured by the
45 capillary rise method using Poiseuille's approximation (Letey et al., 1962), the Washburn equation
46 (Michel et al, 2001; Goebel et al., 2004), or Darcy's law (Emerson and Bond, 1963; Nakaya et al., 1977).
47 The contact angles of the fractions $<63 \mu\text{m}$ and 63 to $100 \mu\text{m}$ for sandy soil measured with the sessile
48 drop method compared reasonably well with those measured with the capillary rise method (Bachmann et
49 al., 2000).

50 However, the influence of surfactant concentration on infiltration in soils has not been evaluated
51 exactly because of the diversity and complexity of soils. Because a surfactant changes water surface
52 tension, the contact angle or wettability of a soil, and the soil hydraulic conductivity, such influences must
53 be evaluated. The purpose of this study is to propose an equation for upward infiltration by capillary
54 action under gravity based on Darcy's law, and to use the equation to determine the effect of an anionic
55 surfactant on infiltration in porous materials. In order to accomplish the latter, we provide a theoretical

56 explanation of the influences of an anionic surfactant on upward infiltration in glass beads, sand, leaf mold,
57 peat moss, and polyethylene particles.

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MATERIALS AND METHODS

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Materials

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Methods

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Upward infiltration experiments were carried out according to the method of Nakaya et al. (1977). The experimental setup used in our study is shown in Fig. 1. Materials were packed into acrylic columns 2 cm in diameter and 60 cm in length. The bottom of the column was covered with filter paper. Four 15-cm-long columns were connected to form the 60-cm-long column. To ensure uniform packing, material was packed into the column in 5-cm layers with the calculated weight in order to assure the prescribed bulk density. The porosity of each material column was calculated from the bulk density and the particle density. Porosities of the packed materials are listed in Table 1. The uniformly packed material column was immersed in the solution. The solution was infiltrated from the bottom, and the distance of the infiltration front from the bottom was measured with a scale attached to the column. Distances to the highest position of the wetting front were determined at 1-minute intervals for a total duration of 20 minutes. The measurement interval was increased gradually after 20 minutes. The solution surface in

90 which the material column was immersed was maintained at $0.2 \text{ m} \pm 2 \text{ mm}$ above the bottom of the
91 column during the experiment by manually adding solution. The experiment was conducted at 25°C . The
92 upward infiltration experiment for each material was not replicated as the result (see Fig. 2) showed good
93 characteristics as described in the RESULTS AND DISCUSSION section.

94 SDS was used because it has a simple structure, with an alkyl group and a negative charge. An anionic
95 surfactant was chosen because many detergents are anionic and commonly anions are supposed to be less
96 adsorptive than cations on soils. The SDS solutions were infiltrated into the experimental column, at
97 concentrations of 0, 3.5, 7.0, 21, 70, and 700 mol m^{-3} . The critical micelle concentration (CMC) was 8.2
98 mol m^{-3} at 25°C (Chemical Society of Japan, 1984). In order to avoid any concentration change at an
99 infiltration front caused by adsorption, a much larger SDS concentration, 700 mol m^{-3} , than CMC was
100 applied as one of the conditions. Surface tension of the solution was measured using the Wilhelmy method,
101 and viscosity was measured with a rotation viscometer (Hiemenz, 1986). The measurement of surface
102 tension was duplicated and that of viscosity was triplicated. The averaged values are listed in Table 2.
103 Ethanol was also infiltrated in order to calculate advancing contact angles for the SDS solutions (Letey et
104 al., 1962). The calculation method is given in the UPWARD INFILTRATION THEORY section using
105 Eq.[3].

106 Swelling experiments were carried out in order to detect swelling phenomena during infiltration. The
107 materials were packed into a 10-cm-thick layer in the acrylic columns 2 cm in diameter. The bottom of the
108 column was covered with filter paper. The densities of the packed materials were the same as those used in
109 the upward infiltration experiments. Pure water or 700 mol m^{-3} SDS solution was infiltrated into each
110 material column by capillary action and hydraulic head, and the column was saturated with the liquid until
111 the water surface was observed on the upper surface of the material column. That is, the hydraulic head
112 was generated beyond the height of the material column. After saturation was reached, the material
113 thickness in the column was measured. The measurement was done once for each material.

114 The saturated material column prepared in the swelling experiment was used for the measurement of
115 saturated hydraulic conductivity, which was conducted using the falling head method (Klute and Dirksen,
116 1986). The measurement was taken three times for each column. The measured values are given in Table
117 3.

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119

UPWARD INFILTRATION THEORY

120 A fundamental upward infiltration equation is derived from the following Darcy's law (Emerson and
121 Bond, 1963; Nakaya et al., 1977).

122

$$q = \varepsilon v = \varepsilon \frac{dx}{dt} = k \frac{\Delta H}{x} \quad [1]$$

123 where q is the water flux density ($\text{m}^3 \text{m}^{-2} \text{s}^{-1}$), ε is the volumetric water content ($\text{m}^3 \text{m}^{-3}$), v is the pore water
 124 velocity (m s^{-1}), x is the distance of the infiltration front from the inflow boundary of the column (m), t is
 125 time (s), k is the saturated hydraulic conductivity (m s^{-1}), and ΔH is the hydraulic head difference between
 126 the inflow boundary and the infiltration front (m).

127 When we adopt the conditions of the upward infiltration experiment to Eq.[1], we get

$$128 \quad \varepsilon \frac{dx}{dt} = k \frac{L+h-x}{x} \quad [2]$$

$$129 \quad h = \frac{2\gamma \cos \theta}{\rho g r} \quad [3]$$

130 where L ($= 0.2 \text{ m}$) is the depth of the bottom of the column from the water surface, h is the suction at the
 131 infiltration front during infiltration (m), γ is the surface tension of the solution (N m^{-1}), θ is the advancing
 132 contact angle ($^\circ$), ρ is the density of the solution (kg m^{-3}), g is the gravitational acceleration (9.81 m s^{-2}),
 133 and r is the equivalent pore radius in the material column (m). Solving Eq.[2] under the condition when
 134 $x=0$ at $t=0$ and $x=x$ at $t=t$, we get

$$135 \quad \frac{\varepsilon}{k} [-x - (h+L) \log|-x + (h+L)| + (h+L) \log(h+L)] = t \quad [4]$$

136 It should be noted that for a cylindrical tube, it can be shown that Eq.[4] is equivalent to the Washburn
 137 equation. The average velocity in a cylindrical tube, v , is

$$138 \quad v = \frac{\rho g r^2}{8\mu} \frac{\Delta H}{x} \quad [5]$$

139 where r is the radius of the cylinder (m), and μ is the viscosity of the liquid (Ns m^{-2}). Substituting Eq.[5]
 140 into Eq.[1], we get

$$141 \quad k = \frac{\varepsilon \rho g r^2}{8\mu} \quad [6]$$

142 When we consider $L=0 \text{ m}$ and substituting Eq.[6] into Eq.[4], we get the following Washburn equation
 143 (Marmur, 2003).

$$144 \quad \frac{\rho g r^2}{8\mu h} t = -\frac{x}{h} - \log\left(1 - \frac{x}{h}\right) \quad [7]$$

145 That is, this newly derived upward infiltration equation [4] is physically equivalent to the Washburn
 146 equation. Saturated hydraulic conductivity, k , does not explicitly appear in the Washburn equation.
 147 However, the new equation [4] contains k . Therefore, k can be determined by using the new equation [4]
 148 as described later. Validity of the new equation [4] can be also evaluated by comparing calculated k with
 149 measured k .

150 The advancing contact angle, θ , can be calculated from Eq.[3] when h and γ are known. The values h
 151 and ε/k in Eq.[4] can be assumed to be constant values during saturated infiltration (Emerson and Bond,

152 1963; Hillel, 1980; Tabuchi, 1995). These values were determined by best fitting x and t with the
153 experimental values. The value r in Eq.[3] was derived from the upward infiltration experiment for
154 ethanol and calculation with Eq.[4], provided θ is 0 for ethanol (Letey et al., 1962): the r was calculated
155 with the derived h and Eq.[3]. The calculated r and h for each material are listed in Table 1 and the
156 calculated θ is listed in Table 2. The h values indicate the suction at the infiltration front during infiltration
157 as defined before.

158 Saturated hydraulic conductivity, k , in the upward infiltration experiment was evaluated using the
159 derived value ε/k . In this calculation, porosity that was already derived was used instead of ε , assuming it
160 was almost equal to ε .

161

162

RESULTS AND DISCUSSION

163

Validity of the Upward Infiltration Equation

164 The proposed upward infiltration equation [4] is a Green-Ampt Type equation. This type of equation
165 has been found to apply quite satisfactorily for cases of infiltration into initially dry coarse-textured soils
166 (Hillel, 1980). For cases of upward infiltration into dry sand, this type of theory agrees well with the
167 experimental data collected when a saturated condition is maintained (Emerson and Bond, 1963; Tabuchi,
168 1995). When the infiltration front rises to some extent, large pore cells will become unsaturated and small
169 pore cells will be saturated (Emerson and Bond, 1963). Then the suction at the infiltration front, h , the
170 volumetric water content, ε , and the hydraulic conductivity, k , will change. Because we intend to apply the
171 proposed upward infiltration equation [4] to saturated infiltration, the fitted parameters h and ε/k in Eq.[4]
172 are constant during infiltration in the calculation. This condition cannot be applied to unsaturated
173 infiltration. Saturated infiltration occurs only in the initial stage. Therefore, we calculated x and t by best
174 fitting them with the measured values of the initial stage using Eq.[4].

175 The measured data and the calculated values for the upward infiltration experiments are shown in Fig.
176 2. The height of the infiltration front in Fig. 2 denotes the distance from the fixed water table as described
177 in Fig. 1. The calculated values fitting the measured data are denoted by solid lines. Dotted lines
178 continuing from the solid lines are calculated values by using the same equations as that used for the
179 calculation of the solid lines. The dotted lines deviate from the measured data. The later deviation between
180 calculated and measured values was probably due to unsaturated conditions. The lines are fitted with the
181 measured values for 0 mol m^{-3} , 7 mol m^{-3} , 70 mol m^{-3} , and 700 mol m^{-3} SDS solutions. Fig. 2 shows that
182 the solid lines agree well with measured data. Standard deviations of the heights of infiltration fronts and
183 correlation ratios of the heights over time for solid lines were calculated from measured values. Standard
184 deviations are less than 1 cm. Correlation ratios are higher than 0.96 except for leaf mold at 700 mol m^{-3}
185 and polyethylene particles at 21 mol m^{-3} ; correlation ratio of the former is 0.888 and that of the latter is

186 0.669.

187 However, a physical parameter such as saturated hydraulic conductivity must be checked to see
188 whether the infiltration equation is of value. The measured and calculated saturated hydraulic
189 conductivities are listed in Table 3. The calculated values at 0 mol m^{-3} are similar to the measured values;
190 measured values for polyethylene particles are not available because water was not able to infiltrate under
191 these conditions. The calculated values at 700 mol m^{-3} for glass beads, sand, peat moss, and polyethylene
192 particles almost agree with the measured values, but that for leaf mold is 45 times larger than the
193 measured value. Therefore, the calculated line for leaf mold at 700 mol m^{-3} is wrong.

194 The large difference between measured and calculated hydraulic conductivities for leaf mold is
195 probably caused by swelling. The expansion ratio, the ratio of increased thickness to the initial thickness
196 of the material column in the swelling experiment, for 700 mol m^{-3} SDS solution is 4.3 % larger than that
197 for pure water; initial thickness is 10.0 cm, saturated thickness with water is 10.4 cm, and saturated
198 thickness with 700 mol m^{-3} SDS solution is 10.83 cm. The difference is much larger than that noted with
199 the other materials (Table 3). When the soil swells, larger pores tend to become smaller and soil
200 permeability decreases.

201 The measured saturated hydraulic conductivities at 700 mol m^{-3} for the other materials are smaller
202 than those at 0 mol m^{-3} because the liquid viscosity of 700 mol m^{-3} SDS solution is 2.1 times larger than
203 that of pure water; the saturated hydraulic conductivity is inversely proportional to the viscosity, as shown
204 in Eq.[6]. Conversely, saturated hydraulic conductivity values are similar among SDS solutions at equal to
205 or less than 70 mol m^{-3} , because these solutions have very similar viscosities (Table 2). Calculated
206 saturated hydraulic conductivities for glass beads and sand are almost the same. For leaf mold,
207 conductivities are similar at 0 mol m^{-3} , 3.5 mol m^{-3} , and 7 mol m^{-3} . When saturation, water flow path, and
208 liquid viscosity are the same among different SDS solutions, hydraulic conductivity is a constant value.
209 However, for leaf mold at 21 mol m^{-3} and 70 mol m^{-3} the value does not remain constant. This result
210 indicates that pore structure changes when concentration exceeds 7 mol m^{-3} , and that the swelling of leaf
211 mold probably affects pore structure. In fact, upward infiltration becomes considerably slower at
212 concentrations greater than 7 mol m^{-3} (Fig. 2(c)). For hydrophobic materials (polyethylene particles and
213 peat moss), the calculated hydraulic conductivities fluctuate among different SDS concentrations. These
214 results probably indicate the differences in saturation and water flow path at different concentrations,
215 because infiltration into smaller pores may become difficult when the obtuse contact angle becomes larger.

216 The hydraulic conductivity and correlation ratio results show that the upward infiltration equation is
217 very appropriate for glass beads and sand. It is also appropriate for leaf mold at equal to and less than 7
218 mol m^{-3} , peat moss at 0 mol m^{-3} and 700 mol m^{-3} , and polyethylene particles at 700 mol m^{-3} .

219

Calculation of Contact Angle

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221
222 The calculated advancing contact angles derived with the upward infiltration equation are listed in
223 Table 2. Several contact angles are omitted in Table 2 for cases in which the upward infiltration equation is
224 not appropriate. Those for leaf mold at 21 mol m⁻³, 70 mol m⁻³, and 700 mol m⁻³ are omitted because the
225 pore structures changed during infiltration due to swelling. That for peat moss at 70 mol m⁻³ is omitted
226 because it could not be calculated: $\cos \theta$ in Eq.[3] became larger than 1.0 in calculation. As noted in the
227 UPWARD INFILTRATION THEORY section, the contact angle, θ , can be calculated from Eq.[3] when h
228 and γ are known. h is determined by a best fit of the measured values. γ used in these calculations, along
229 with the resulting θ (shown with no parentheses or dagger), for each SDS concentration are listed in Table
230 2. For calculations using the surface tension of pure water ($\gamma=72$ mN m⁻¹), a dagger was added to the
231 resulting θ . For calculations made with both the γ for pure water and that corresponding to the SDS
232 concentration, parentheses are added to θ values in Table 2.

233 When SDS is adsorbed on a material, the concentration of the infiltration front is smaller than the
234 influent concentration. The influence on γ must be considered in this case. Because SDS has a
235 hydrophobic tail, adsorption by hydrophobic interaction occurs in organic materials. Therefore, the
236 influence is considered for leaf mold, polyethylene particles, and peat moss. The influence must be
237 considered for sand because it has 0.5% organic matter. In fact, the measured heights of the infiltration
238 front for 0 mol m⁻³, 3.5 mol m⁻³, 7 mol m⁻³, and 21 mol m⁻³ solutions are almost the same for sand (Fig.
239 2(b)). In these cases, the SDS concentration at the infiltration front was supposed to become almost 0 mol
240 m⁻³, because SDS was adsorbed on sand during infiltration. Then their infiltration rates became similar.
241 For leaf mold, the measured heights of the infiltration front for 0 mol m⁻³ and 3.5 mol m⁻³ solutions are
242 almost the same (Fig. 2(c)) due to the effect of adsorption. Therefore, $\gamma=72$ mN m⁻¹ was also used for
243 calculating θ for 3.5 mol m⁻³ solution. In leaf mold for 7 mol m⁻³ solution, the result was the same when
244 either $\gamma=72$ mN m⁻¹ or $\gamma=38$ mN m⁻¹ was used, because θ was 90°. For both peat moss and polyethylene
245 particles, both surface tensions of pure SDS concentrations and $\gamma=72$ mN m⁻¹ were used, because the
246 concentrations at the infiltration fronts were unknown. The expected contact angle ranges are listed in
247 parentheses in Table 2 in these cases. In addition, as mentioned in the Validity of the Upward Infiltration
248 Equation section, the calculated hydraulic conductivities under these conditions fluctuate. These results
249 indicate differences in saturation and water flow path at different concentrations. Because the calculation
250 of θ is based on the same saturation and water flow path conditions as that for ethanol infiltration, these
251 calculated values are not very reliable.

252 The methods of contact angle calculation which use this upward infiltration equation and the
253 Washburn equation are not highly reliable because water flow in porous materials is complicated and the

254 advancing contact angle of low surface tension liquid is not always 0° (Siebold, 2000). However, these
255 methods are preferable to any technique for porous materials. (Hiemenz, 1986).

256

257 **Influence of Wettability on Infiltration of Pure Water and 700 mol m^{-3} SDS Solution**

258 The measured heights of infiltration front for pure water (Fig. 3) are in the descending order of glass
259 beads > sand > leaf mold > peat moss > polyethylene particles; the smaller advancing contact angle of the
260 material, the higher is the infiltration front (Table 2). This result indicates that the influence of contact
261 angle or wettability is larger than the differences in average particle sizes (Table 1). At an early stage, the
262 heights of infiltration front for glass beads are smaller than those for sand, probably because of the smaller
263 pores for glass beads: saturated hydraulic conductivity becomes smaller with smaller pores. Pure water
264 infiltrates well into hydrophilic materials and infiltrates poorly into hydrophobic materials. Pure water
265 cannot infiltrate into the polyethylene particles even at a 20-cm water head. Nakaya et al. (1977) indicated
266 that the height of infiltration front decreased with the increase in coated humic acid on quartz sand.
267 Because the coating of humic acid increases hydrophobicity, this result agrees with our result. The
268 measured height for peat became larger than 0 cm after 200 min even though the calculated contact angle
269 is 99° . This result indicates that the peat surface at the infiltration front became hydrophilic during
270 measurement. Michel et al. (2001) demonstrated the change from hydrophilicity to hydrophobicity during
271 desiccation of peat. Our result corresponds to their result.

272 Conversely, the measured heights of infiltration fronts for 700 mol m^{-3} SDS solution are similar for all
273 media except for leaf mold (Fig. 4). The surfactant, which is amphipathic, decreased the contact angles for
274 the hydrophobic materials, and the contact angles became similar among the materials (Table 2). Even
275 hydrophobic materials become wettable with surfactant.

276 The height of infiltration front in leaf mold for 700 mol m^{-3} SDS solution is by far the lowest due to
277 the very low level of saturated hydraulic conductivity (See the measured value in Table 3), which is
278 probably caused by swelling. Such structural change in the leaf mold restricted solution infiltration.

279

280

Impact of SDS Concentration

281 **Effect of Surface Tension**

282 For the hydrophilic materials (glass beads and sand) the heights of infiltration fronts decrease with
283 increasing SDS concentration because of the decrease in suction (Fig. 2(a), (b)). The suction decreases
284 with the increase of SDS concentration, because the surface tension decreases with the increase in SDS
285 concentration; the relationship between suction and surface tension is given in Eq.[3]. Because the
286 advancing contact angles do not differ much among different SDS concentrations (see in Table 2), surface
287 tension affects infiltration considerably. These results agree with the results obtained by Pelishek et al.

288 (1962) who used a wetting agent for quartz sand. However, they did not compare different concentrations
289 of wetting agent.

290 For leaf mold, the height of infiltration front also decreases with increasing SDS concentration (Fig.
291 2(c)). The contact angle for 0 mol m^{-3} is 84° , slightly acute. Therefore, the decrease of surface tension with
292 the concurrent increase of SDS concentration may cause the decrease in height. However, the influence of
293 swelling is supposed to be more significant when the concentration increases.

294 For hydrophobic materials (polyethylene particles and peat moss) the heights of infiltration fronts
295 increase with increasing SDS concentration because of the increase in suction, except for 700 mol m^{-3}
296 SDS solution (Fig. 2(d),(e)). The suction increases with the increase in SDS concentration, because the
297 surface tension decreases with the increase in SDS concentration and $\cos \theta$ is negative when θ is obtuse;
298 the relationship between suction and surface tension is given in Eq.[3]. The influence of suction on the
299 height of infiltration front is depicted in Fig. 5. The solid lines are the calculated values with the same
300 $\theta(=110^\circ)$ and a different γ . In the calculations with Eq.[4], $\varepsilon/k = (\varepsilon/k)_{700} \times (0.89/1.89)$ was used. $(\varepsilon/k)_{700}$
301 is the obtained value when the calculated values were fitted with the measured values at 700 mol m^{-3} SDS
302 solution. The data for 700 mol m^{-3} SDS solution are supposed to be most suitable because the material
303 becomes wettable. Therefore, $(\varepsilon/k)_{700}$ was chosen. However, the solution viscosity was modified to 0.89
304 Pa·s by multiplying by $0.89/1.89$ in order to compare the data for 0 to 70 mol m^{-3} SDS solution. The
305 calculated result indicates that the height increases with the decrease in surface tension. However, the
306 change in surface tension cannot completely explain the increased height; the measured increase is much
307 larger than the calculated increase. In the case of 700 mol m^{-3} SDS solution, the height is smaller in the
308 initial stages due to the high viscosity, as mentioned before. In the later stages, the heights of infiltration
309 fronts become highest for polyethylene particles and the second highest for peat moss, because of the
310 wettability.

311

312 **Effect of Contact Angle**

313 For the hydrophilic materials (glass beads and sand), the advancing contact angles differ little among
314 different SDS concentrations (see in Table 2). For sand, they are almost same from 0 mol m^{-3} to 70 mol
315 m^{-3} . For glass beads, there is no simple increase or decrease with increasing SDS concentration. As
316 discussed before, the contact angles are not a major cause of the decrease in height of infiltration front
317 with the increase in SDS concentration. For the leaf mold, because the contact angles are around 90° for 0
318 mol m^{-3} , 3.5 mol m^{-3} and 7 mol m^{-3} solutions, their influence following the change in SDS concentration is
319 also not significant. At concentrations higher than 7 mol m^{-3} for leaf mold, the effect of swelling is
320 supposed to be most significant, as discussed before.

321 For the hydrophobic materials (polyethylene particles and peat moss), the effect of contact angles are

322 significant. The contact angles for these materials become smaller with an increase in SDS concentration,
323 which causes the increase in height of the infiltration front. The materials become wettable with increasing
324 SDS concentration, because the surfactant is amphipathic. In Fig. 6, the measured heights of infiltration
325 fronts and those calculated with $\gamma=38 \text{ mN m}^{-1}$, in addition to the different advancing contact angle in the
326 polyethylene particles, are shown. In the calculations with Eq.[4], $\varepsilon/k = (\varepsilon/k)_{700} \times (0.89/1.89)$ was also used
327 in order to compare the data for 0 to 70 mol m⁻³ SDS solution, as mentioned before. The result clearly
328 shows that the influence of the contact angle on the height is significant. In fact, the obtained advancing
329 contact angles for 700 mol m⁻³ SDS ($\theta=69^\circ$ for polyethylene particles, $\theta=43^\circ$ for peat moss) are much
330 smaller than those for 0 mol m⁻³ SDS ($\theta>125^\circ$ for polyethylene particles, $\theta=102^\circ$ for peat moss). Pelishek
331 et al. (1962) showed a similar effect of the wetting agent on infiltration in the materials whose contact
332 angles with pure water were 72° and 83° . We also show that a decrease in surface tension with an increase
333 in the SDS concentration also increases the height of the infiltration front.

334

335

Influence of Adsorption

336 Anionic surfactants adsorb on soils via hydrophobic interaction (Atay et al., 2000). The adsorption
337 affected infiltration rate in our experiment. In sand for 3.5, 7.0 and 21 mol m⁻³ SDS solution and leaf mold
338 for 3.5 mol m⁻³ SDS solution, the heights of infiltration fronts become almost the same as those for 0 mol
339 m⁻³ SDS solution. These results suggest an influence of SDS adsorption on the materials, as previously
340 noted. The retardation of anionic surfactant from the wetting front due to adsorption in loamy sand was
341 reported by Allred and Brown (1996). In our research, the SDS concentration of the infiltration front is
342 supposed to decrease due to adsorption on the soils, and then surface tension increases. Thus the
343 infiltration rate of the SDS solution becomes the same as that of pure water. In peat moss, the influence of
344 adsorption on the height is observed at 3.5 mol m⁻³; the height for 3.5 mol m⁻³ SDS solution is similar to
345 that for 0 mol m⁻³ SDS solution (Fig. 2(e)).

346 In leaf mold, the saturated hydraulic conductivity decreases when the SDS solution at a higher
347 concentration infiltrates. The swelling of the material induces a decrease in hydraulic conductivity. The
348 increases in the heights of infiltration fronts for 21 mol m⁻³ and 70 mol m⁻³ SDS are restricted in the initial
349 stages, and that for 700 mol m⁻³ is restricted in all stages (Fig. 2(c)). These trends are probably due to the
350 low saturated hydraulic conductivity caused by swelling. The heights for 21 mol m⁻³ and 70 mol m⁻³ SDS
351 increase at the later stage, probably because the concentrations are too low for enough adsorption to
352 generate sufficient swelling and maintain low hydraulic conductivity. The swelling mechanism for leaf
353 mold can probably be attributed to electrostatic repulsive force caused by adsorbed anionic surfactant.
354 However, more research is needed to clarify this point.

355 Hydraulic conductivity reductions for loam (Allred and Brown, 1994) and silty clay loam (Liu and

356 Roy, 1995) caused by SDS were reported by other researchers. Liu and Roy (1995) suggested that the
357 reduction was mainly caused by the Ca surfactant precipitation. In our experiment, however, the
358 precipitation with divalent cations such as Ca did not occur because divalent cations had been removed
359 before the experiment.

360 Conversely, the measured hydraulic conductivity of peat moss for 700 mol m^{-3} does not become much
361 smaller than that for 0 mol m^{-3} , although both peat moss and leaf mold are organic soils. The expansion
362 ratios for peat moss differ little between those at 0 mol m^{-3} SDS and at 700 mol m^{-3} SDS, while those for
363 leaf mold differ quite noticeably (Table 3). The different results for leaf mold and peat moss probably arise
364 from the difference in adsorption and structural stability.

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SUMMARY AND CONCLUSIONS

367 We proposed an upward infiltration equation based on Darcy's law. The infiltration equation was
368 shown to be equivalent to the Washburn equation. The values calculated using the equation showed good
369 agreement with the measured infiltration values, especially for the inorganic materials (glass beads and
370 sands).

371 By using the new equation, we evaluated the influence of the anionic surfactant (SDS) on infiltration
372 in porous materials. Saturated hydraulic conductivity and the material expansion ratio were also measured
373 for the evaluation. Consequently, the infiltration could be explained well theoretically using values for
374 surface tension and contact angle, which are affected by SDS concentration.

375 In glass beads and sand, which are hydrophilic inorganic materials, the infiltration rate decreased as
376 the SDS concentration increased due to the decrease in solution surface tension. No major change in the
377 contact angle was observed. The upward infiltration equation explained this infiltration well. In
378 polyethylene particles and peat moss, which are hydrophobic organic materials, the infiltration rate
379 increased as the SDS concentration increased because of the decrease in the contact angle and surface
380 tension.

381 In leaf mold, the saturated hydraulic conductivity became much lower at higher SDS concentrations,
382 whereas in peat moss, also an organic material, such change was not observed. Their surface
383 characteristics may differ with respect to interaction with an anionic surfactant. Further investigation is
384 needed to clarify this point.

385 Because soils are diverse and complex, the influence of surfactants on infiltration may vary. The
386 simple experiments and the upward infiltration equation which we applied to the analysis of the
387 experimental data are useful. Since surfactants significantly affect the physicochemical nature of the soil
388 surface, it is worth performing basic research to further understand and improve the technical use of
389 surfactants in applications such as soil remediation. Large amounts of surfactants are discharged as

390 municipal or industrial wastes. Moreover, most organic compounds are surface-active in aqueous solution.
391 Therefore, those surfactants could potentially influence water flow in soils.

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Figure Captions

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- 468 Fig. 1 Schematic diagram of the setup for upward infiltration experiment.
- 469
- 470 Fig. 2 Height of infiltration front during upward infiltration of SDS (sodium dodecyl sulfate) solution.
- 471 Symbols are measured values. Solid lines are calculated values fitted with measured data. Dotted lines are
- 472 calculated values that follow solid lines. The lines are fitted with the measured values for 0 mol m^{-3} , 7 mol
- 473 m^{-3} , 70 mol m^{-3} and 700 mol m^{-3} SDS solutions.
- 474
- 475 Fig. 3. Height of infiltration front during pure water infiltration.
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- 477 Fig. 4. Height of infiltration front during 700 mol m^{-3} SDS solution infiltration.
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- 479 Fig. 5. Height of infiltration front in the polyethylene particles column. Solid lines are the calculated
- 480 curves with different surface tensions and the same advancing contact angle ($\theta=110^\circ$).
- 481
- 482 Fig. 6. Height of infiltration front in the polyethylene particles column. Solid lines are the calculated
- 483 curves with different advancing contact angles and the same surface tension ($\gamma=38 \text{ mN m}^{-1}$).
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Table 1. Physical properties of the materials used for the upward infiltration experiments.

Material	Mean radius	Particle density	Porosity	Organic [†] matter	Equivalent pore radius	Suction h	
						0 mol m ⁻³ SDS [‡]	700 mol m ⁻³ SDS [‡]
	mm	g cm ⁻³	%	%	mm	cm	cm
Glass beads	0.06	2.47	40.5	0	0.027	21.8	6.97
Sand	0.18	2.67	46.9	0.5	0.034	13.6	6.17
Leaf mold	0.15	1.75	74.9	100	0.080	2.5	—
Peat moss	0.12	1.55	91.6	100	0.050	-3.5	5.56
Polyethylene particles	0.08	0.93 [†]	35.5	100	0.042	< -20	6.37

[†]Data from producers

[‡]SDS, sodium dodecyl sulfate

Table 2. Calculated advancing contact angles, surface tensions and viscosities of SDS solutions. Contact angles in () were calculated using the surface tensions at 0 mol m⁻³ and the influent concentration because the concentration at the infiltration front was unknown.

	SDS concentration					
	0 mol m ⁻³	3.5 mol m ⁻³	7 mol m ⁻³	21 mol m ⁻³	70 mol m ⁻³	700 mol m ⁻³
Advancing contact angle						
Glass beads	36°	30°	28°	43°	45°	60°
Sand	51°	50°†	52°†	50°†	49°	57°
Leaf mold	82°	85°†	90°	—	—	—
Peat moss	102°	(112-124°)	(101-110°)	(94-97°)	—	43°
Polyethylene particles	>125°	(107-117°)	(109-127°)	(103-116°)	(92-93°)	69°
Surface tension	mN m ⁻¹	72	47	39	38	38
Viscosity	Pa s	0.89	—	—	0.91	0.99
Solution density	kg m ⁻³	1.00x10 ³	1.00 x10 ³	1.00 x10 ³	1.00 x10 ³	1.03 x10 ³

† calculated with $\gamma=72$ mN m⁻¹

Table 3. Expansion ratios and measured saturated hydraulic conductivities of the material columns with 10-cm length, and calculated saturated hydraulic conductivities.

SDS conc.	Expansion ratio		Measured saturated hydraulic conductivity		Calculated saturated hydraulic conductivity					
	- mol m ⁻³ -		- mol m ⁻³ -		mol m ⁻³					
	0	700	0	700	0	3.5	7	21	70	700
	- % -		- cm s ⁻¹ -		cm s ⁻¹					
Glass beads	-0.3	-0.3	1.1×10 ⁻²	3.2×10 ⁻³	7.4×10 ⁻³	6.8×10 ⁻³	7.3×10 ⁻³	8.3×10 ⁻³	6.8×10 ⁻³	2.3×10 ⁻³
Sand	-0.1	-1.3	3.0×10 ⁻²	7.5×10 ⁻³	3.3×10 ⁻²	3.4×10 ⁻²	2.9×10 ⁻²	2.8×10 ⁻²	3.1×10 ⁻²	7.9×10 ⁻³
Leaf mold	4.0	8.3	1.6×10 ⁻²	4.9×10 ⁻⁴	1.5×10 ⁻²	1.5×10 ⁻²	1.3×10 ⁻²	6.0×10 ⁻³	2.4×10 ⁻²	2.2×10 ⁻²
Peat moss	3.7	4.3	1.3×10 ⁻²	8.2×10 ⁻³	1.3×10 ⁻²	2.7×10 ⁻²	4.2×10 ⁻²	3.4×10 ⁻²	2.1×10 ⁻²	4.1×10 ⁻³
Polyethylene particles	-	2.7	-	3.8×10 ⁻³	-	1.6×10 ⁻³	3.9×10 ⁻³	6.5×10 ⁻³	1.2×10 ⁻²	2.2×10 ⁻³

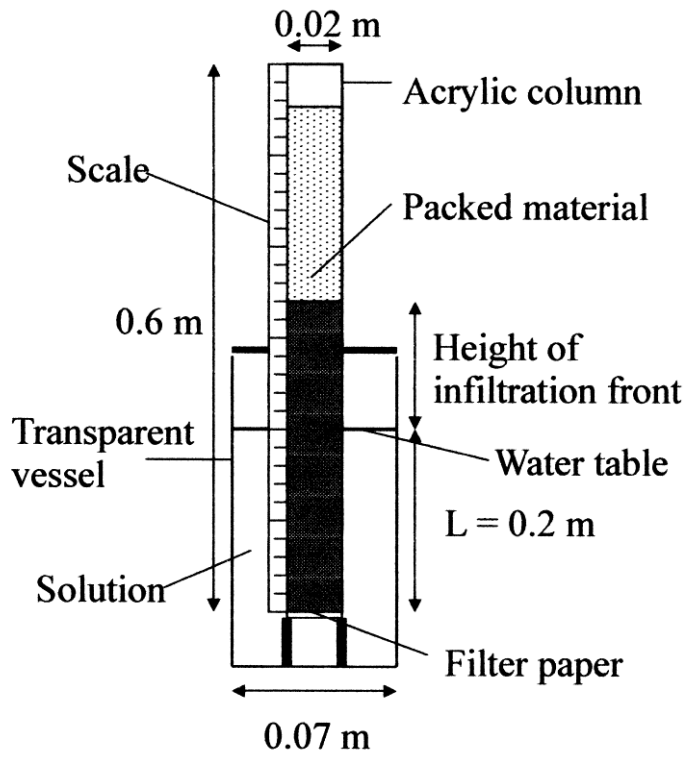


Fig. 1 Schematic diagram of the setup for upward infiltration experiment.

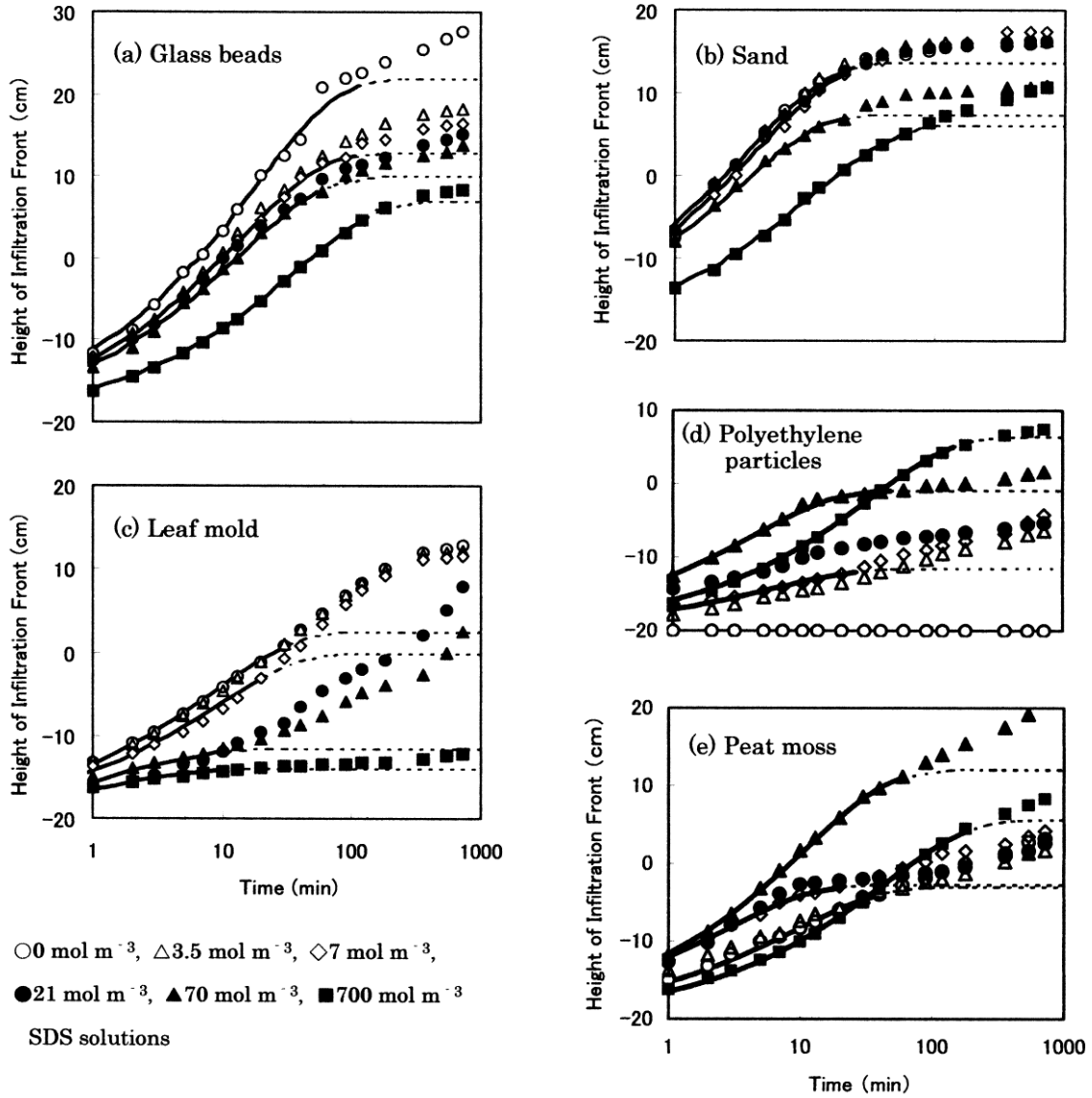


Fig. 2 Height of infiltration front during upward infiltration of SDS (sodium dodecyl sulfate) solution. Symbols are measured values. Solid lines are calculated values fitted with measured data. Dotted lines are calculated values that follow solid lines. The lines are fitted with the measured values for 0 mol m^{-3} , 7 mol m^{-3} , 70 mol m^{-3} and 700 mol m^{-3} SDS solutions.

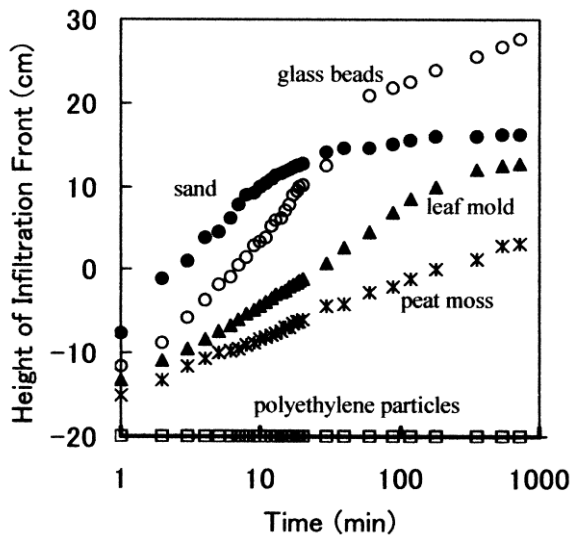


Fig. 3. Height of infiltration front during pure water infiltration.

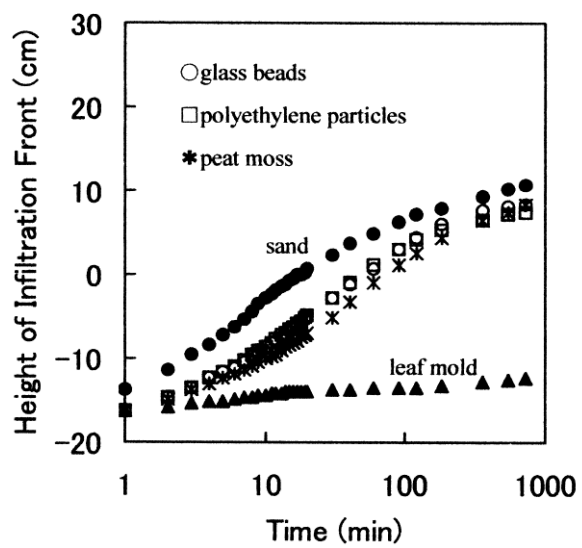


Fig. 4. Height of infiltration front during 700 mol m^{-3} SDS solution infiltration.

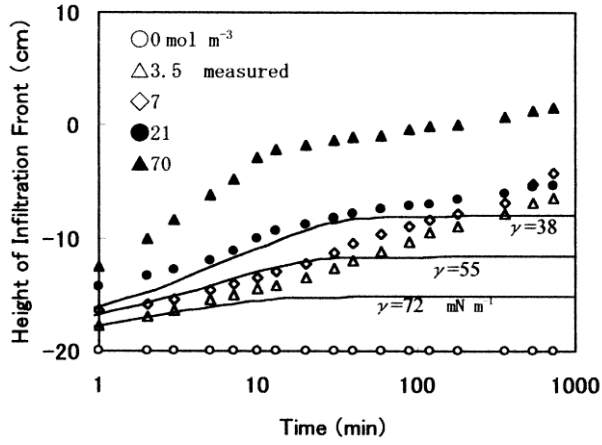


Fig. 5. Height of infiltration front in the polyethylene particles column. Solid lines are the calculated curves with different surface tensions and the same advancing contact angle ($\theta=110^\circ$).

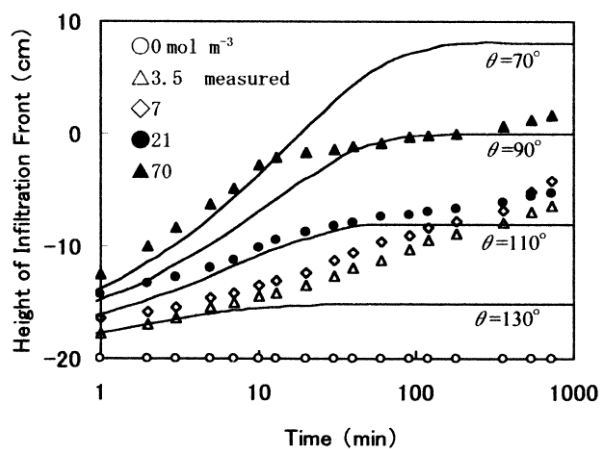


Fig. 6. Height of infiltration front in the polyethylene particles column. Solid lines are the calculated curves with different advancing contact angles and the same surface tension ($\gamma=38 \text{ mN m}^{-1}$).