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On the Transport of Emulsions in Porous Media

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Abstract

Emulsions appear in many subsurface applications including bioremediation, surfactant-enhanced remediation, and enhanced oil-recovery. Modeling emulsion transport in porous media is particularly challenging because the rheological and physical properties of emulsions are different from averages of the components. Current modeling approaches are based on filtration theories, which are not suited to adequately address the pore-scale permeability fluctuations and reduction of absolute permeability that are often encountered during emulsion transport. In this communication, we introduce a Continuous Time Random Walk based alternative approach that captures these unique features of emulsion transport. Calculations based on the proposed approach resulted in excellent match with experimental observations of emulsion breakthrough from the literature. Specifically, the new approach explains the slow late-time tailing behavior that could not be fitted using the standard approach. The theory presented in this paper also provides an important stepping stone towards a generalized self-consistent modeling of multiphase flow.

Key words: emulsion, porous media, colloidal transport, memory effects
1 Motivation

Transport [1] of (micro)emulsions in porous media is relevant to several subsurface applications. Nearly all enhanced oil recovery processes involve emulsion formation and flow in some form or other [1]. Recently, it has been shown that emulsification of edible oils prior to injection into groundwater (as a substrate for enhanced bioremediation) improves its spatial distribution in the contaminated zone [2,3]. Subsurface uses of microemulsions, which posses large interfacial area and have the ability to solubilize otherwise immiscible liquids [4], include cleanup of chlorinated solvents from groundwater [5] and enhanced oil-recovery [6–8].

Emulsion transport in porous media can be broadly classified according to (a) the stability of the emulsion and (b) the drop size of the dispersed phase relative to the pore size of the medium [9]. One class involves dilute, relatively unstable emulsion with very small average drop-size to pore-size ratio. A second class involves relatively stable emulsions with drop-size to average pore-size ratio on the order of unity. A third class, which is the subject of this paper, involves stable emulsions with relatively small drop-size to average pore-size ratio.

Current approaches of modeling the latter class of emulsions capitalize on the similarity of the transport and attachment-detachment processes of the dispersed-phase droplets with those of colloids [10,3]. In general, most colloidal transport models are extensions of the advection-dispersion equation (ADE), which assumes colloid and grain size homogeneity at all scales. As

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a result, these models predict a fast exponential concentration decay and do not capture slow late-time elution of colloids satisfactorily. Recently, we introduced a Continuous Time Random Walk (CTRW) based filtration model for biocolloid transport [11] that captures small-scale heterogeneity in an effective stochastic framework. The proposed approach provided excellent match with experimental breakthrough curves, including the late-time slow tailing. The objective of this communication is to extend the CTRW based approach to the transport of emulsions.

2 Theoretical Considerations

Soo and Radke [10] described the transport of emulsion in porous media as analogous to transport of a colloidal phase. Transport of colloids is commonly modeled by colloid filtration theory (CFT) [12] as an extension of the ADE

\[
\frac{\partial c}{\partial t} + \frac{\rho_b \theta}{\theta} \frac{\partial s}{\partial t} = F[c(x, t)],
\]

where lengths are made non-dimensional with respect to the column length \( L \),

\[
F[c(x, t)] \equiv -v \left[ \lambda c + \frac{\partial c}{\partial x} - \alpha \frac{\partial^2 c}{\partial x^2} \right]
\]

is the classical filtration operator (with \( v \) the pore velocity and \( \alpha \) the dispersivity) acting on the colloid concentration \( c(x, t) \), and

\[
\frac{\partial s}{\partial t} = \frac{\theta}{\rho_b} k_f c - k_r s
\]

where \( \theta \) is the porosity, \( \rho_b \) is the colloid density, \( s \) is the colloid concentration adsorbed reversibly on solid surfaces, \( k_f \), and \( k_r \) are the forward and reverse sorption rates, respectively. The parameter \( \lambda \) is the filtration coefficient, the
fraction of irreversibly sorbed dispersed phase, which can be calculated as

$$\lambda = -\ln(f) + \alpha \ln(f^2)$$  \hfill (4)

where $f$ is the eluted fraction [13]. An extensive review of the filtration coefficient $\lambda$ and its parameters can be found in [14] and [15]. Eq. (3) adequately describe the initial advection-dispersion dominated breakthrough, but not the late-time elution of the dispersed phase. Laboratory and field experiments often display power-law decaying of the breakthrough curve tails, which cannot be captured by the ADE-based filtration models that predict an exponential decay of the dispersed-phase concentration. The misrepresentation of the tails is rooted in the definition of the forward and reverse sorption rates in (3) as mean values over some volume. The inherent heterogeneity of natural porous materials, however, induces a wide spectrum of rates, which can only be represented by some probabilistic distribution function (pdf).

Physico-chemical attachment and detachment of the dispersed phase can be attributed to small scale heterogeneities of the pore-surface dispersed-phase properties. In particular, surface charge heterogeneities on both, the dispersed and solid phases play a fundamental role in the transport of the dispersed phase. Furthermore, the dispersed-phase droplets can vary in shape, size, and surface heterogeneity. These multiscale heterogeneities, which are difficult to characterize in a fully deterministic way, call for an ensemble averaged stochastic treatment of the unresolved level of heterogeneity. In order to account for these heterogeneities, we propose a conceptual model that is similar to the filtration model described in (1) to the extent that it decouples the transport of the dispersed phase into advective and dispersive fluxes, and sorption and desorption mechanisms. Whereas the ADE approach ignores the
small heterogeneities, our proposed model treats these in terms of probabilistic
distributions. We have shown elsewhere [11] that a CTRW based filtration-
model provides excellent description of both the advection-dispersion domi-
nated early breakthrough and the late time elution of colloids. CTRW is an
effective stochastic transport theory based on local-scale ensemble averages.
At the core of the CTRW formulation is  \( \psi(t) \), the waiting time pdf for a
single droplet transition over time  \( t \). This function implicitly accounts for all
transport mechanisms (e.g., advection, dispersion, sorption, and desorption)
that displace a particle from one spatial location to another. For an extensive
review of the CTRW in hydrogeological applications see [16] and references
therein. The CTRW filtration equation can be written as

\[
\tilde{u}\tilde{c}(x, u) - c_0(x) = \tilde{M}(u)F[\tilde{c}(x, u)]. \tag{5}
\]

The tilde  \( \tilde{\cdot} \) in Eq. 5 indicates Laplace transformed quantities with respect to
time  \( t \), and  \( u \) is the Laplace variable. The quantity  \( \tilde{M}(u) \) is defined as

\[
\tilde{M}(u) = \tilde{t}u\frac{\tilde{\psi}(u)}{1 - \tilde{\psi}(u)}, \tag{6}
\]

and plays the role of a memory function, which convolutes the classical filtra-
tion operator,  \( F[\tilde{c}(x, u)] \).

Considering the similarity in \( \zeta \)-potentials between bio-colloids and oil droplets
in emulsions, we propose that (5) can be used to effectively describe emulsion
transport in porous media.

Following Margolin et al. [17], we define the waiting time pdf  \( \psi(t) \) (which
describes how the droplets in the dispersed phase are temporarily trapped
and then released after some time  \( t \)) as a generalized convolution integral of
two contributions:  \( \psi_0(t) \), which is related to the complexity of the pore space
geometry, and $\phi(t|\tau)$ (with $\tau = (t - t')/T$), which defines the retention of the dispersed droplets, $\psi(s, \tau) = \int_0^\tau \psi_0(s, \tau - \tau')\phi(\tau'|\tau - \tau')d\tau'$. In the limit $\phi(t|\tau) \equiv \delta(t' - \Lambda \tau)$, Eq. 5 is reduced to an ADE with simple retardation $R = (1 + \Lambda)$. More generally, $\phi(t|\tau)$ accounts for multiple attachment and detachment events of a droplet in the time interval $\tau$, and as such can be defined by means of multiple convolutions of a large number of single “sticking time” pdfs, $\varphi(t)$, (compound Poisson process). Denoting by $\Lambda$ the average free state sticking rate, it is possible to write $\tilde{\varphi}(u) \equiv \exp(\Lambda \tau(\tilde{\varphi}(u) - 1))$. With these definitions, $\tilde{\psi}(u)$ reads as $\tilde{\psi}(u) = \tilde{\psi}_0(u + \Lambda(1 - \tilde{\varphi}(u)))$. When $\tilde{M}(u) = 1$, and $\Lambda = 0$ the CTRW filtration PDE reduces to the classical filtration theory. If $\Lambda > 0$, the memory $\tilde{M}(u) \neq 1$, i.e., the model exhibits memory effects as a result of the time convolution. A detailed account of these developments can be found in [17] and [11].

At this point we introduce some assumptions on the functional forms of $\psi_0(t)$ and $\varphi(t)$. The $\psi_0(t)$ models the impact of pore space heterogeneity on the anomalous tailing of the dispersed phase due to pore shape heterogeneity and accounts for the anomalous tailing in the breakthrough of conservative tracers in homogeneously packed soil columns. To account for pore-level geometric heterogeneity of a passive tracer experiments, it is sufficient to adopt an asymptotic power-law model of the form $\tilde{\psi}_0(u) = 1/(1 + u^\gamma)$ (with $0 < \gamma < 1$), which yields a power law tailing [18]. For homogeneous porous structures, $\gamma$ approaches 1, and the waiting time pdf tends towards an exponential, $\psi_0(t) \sim \exp(-t/\bar{t})$, i.e., passive tracer transport tends toward a Fickian-behavior limit. Small-scale heterogeneities in physico-chemical interactions can also be represented by a sticking time pdf of the form $\tilde{\varphi}(u) \equiv 1/(1 + u^\beta)$, where $0 < \beta < 1$.
From a physical point of view, this means that there is no single characteristic filtration time scale for this problem.

3 Illustrative Example

The experimental results used to illustrate the proposed theory were derived from Coulibaly et al. [3] (experiment FS-7%-#2). The experiment was conducted using a PVC column of length $L = 0.8$ m and diameter $D = 0.029$ m. The column was filled with medium to fine sand ($D_{10} = 0.10$ mm, $D_{50} = 0.38$ mm, $D_{60} = 0.45$ mm, and 6.9% by weight is finer than 75 $\mu$m) dry packed to achieve bulk density of 1.44 kg/m$^3$, equivalent to a porosity of $\theta = 0.46$. The emulsions used in this experiment were prepared by blending 33% by volume soybean oil, 62% tap water, and 5% premixed surfactant (38% polysorbate 80, 56% glycerol monooleate from Lambent Technologies and 6% water) in a commercial blender at high speed for 5 min. The mean droplet size was 1.2 $\mu$m (standard deviation 1.3 $\mu$m). The $\zeta$ potential of the oil droplets and sand in tap water (pH = 8.2 and specific conductance = 190 $\mu$S/cm) were -18 mV and -24 mV, respectively, indicating unfavorable conditions for the negatively charged oil droplets to stick to the negatively charged sand [3].

The column was first evacuated and then saturated by flowing de-aerated water upwards at 2.5 mL/min for 2 hours. Subsequently, a nonreactive transport test was conducted by injecting 25 mL ($\sim 0.1$ PV) of 175 mg/L NaBr solution through the column followed by 1000 mL of deaired water. Effluent samples were analyzed for Br by ion chromatography. The emulsion flow test was conducted by injecting 25 mL of 11% oil by volume emulsion ($\sim 0.05$ PV of pure oil) followed by 1000 mL of deaired water. The effluent was collected every 30
The experimental oil BTC was fitted by means of (5). The time has been rescaled in such a way that the BTC is plotted in pore-volumes. Lengths have been rescaled by the column length $L$. The value of the filtration coefficient $\lambda = 2.72$, was obtained from (4) with the reported eluted fraction, $f = 0.065$ and the value of the dispersivity $\alpha = 0.1$ was obtained from the NaBr tracer test [3]. This non-dimensional value of the dispersivity clearly indicates a scale effect [19]. Considering that the porous medium used in the experiments was made of sand grains of different sizes, it is legitimate to expect significant small-scale heterogeneity of flow and transport properties. Long tailing in the passive tracer BTC, which is typical in such porous media [2], might have been misinterpreted as elevated dispersivity. Therefore, we introduce a model for the $\psi_0(t)$ which assumes a long tailing, i.e., $\gamma < 1$ and a value of the dispersivity of the same order of magnitude of the the median grain diameter-to-column length ratio, $D_{50}/L = 4.75 \times 10^{-4}$. Given the distribution of diameter size

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**Fig. 1.** Comparison of experimental results with model fits at $-2.0$ mL and analyzed for oil content by volatile solids method.
typical of the sand used in the experiment, we selected a value of $\alpha = 1.5 \times 10^{-3} \sim 3D_{50}/L$. A sensitivity analysis indicates the appropriateness of this choice of $\alpha$. In contrast, using the value of $\alpha = 0.1$ reported by Coulibaly et al. [3] and a value of $\gamma = 1$ (Gaussian transport for the passive tracer), results in unsatisfactory CTRW model fit of the experimental BTC. The best fit values of the free parameters are $\Lambda = 0.58$, $\beta = 0.4$, and $\gamma = 0.9$. The relatively high value for $\gamma$ indicates that some geometrical disorder is present in the experimental column, as one would expect for natural soils. The small value of $\beta$ is in agreement with that of transport of bio-colloids [18]. This value for $\beta$ indicates a very high degree of physico-chemical disorder of the surface heterogeneity and a corresponding broad sticking time pdf $\varphi(t)$.

The best fit value for the transport velocity $v$ indicates a retardation factor $R = (1+\Lambda) = 1.58$, in accordance to the sharply peaked $\phi(t, t-t') \sim \delta(t'-\Lambda \tau)$ analyzed earlier. The results are, thus, pointing towards a bi-modal type of transport for the dispersed phase: the first mode explains the attachment and detachment of the oil droplets to the pore walls and is characterized by a power law dominated sticking time pdf, whereas the second mode, clearly indicated by the overall retardation, can be attributed to a film-like flow along the surface of the pores.

4 Open Research Questions

The CTRW based model for emulsion transport introduced in this paper provided an excellent match to the experimental oil BTC of Coulibaly et al. [3]. In particular, the late-time long tailing was shown to be in remarkable agreement with a power-law dominated pdf for attachment and detachment.
of the dispersed-phase (oil). This finding leads to interesting research questions related to multiphase flow in porous media. We have shown here that the long time correlations underlying the power-law dominated pdfs need to be taken into account for a correct description of emulsion transport. The consequences of this microscopic behavior on other measurable macroscopic parameters needs further exploration.

We also recognize that the permeable pore space available for water flow is continuously changed as oil-droplets are lodged in pore-throats and pore-walls, resulting in transient effects in the small scale permeability to water. This effect is different from straining of rigid colloids because the capillary forces that keep emulsion droplets in place can be readily overcome by hydrodynamic stresses. Moreover, the oil droplets in the dispersed phase inside the pore space are continuously moving giving the water phase a moving boundary for its flow. Recalling that the permeability of a porous medium at Darcy scale ($k_0$) is defined as the volume average of the Stokes velocity flow field in the pore space available to the water phase, it becomes evident that when the fluctuation of the local $k$ value (with respect to $k_0$) are correlated in time, can induce macroscopically measurable changes in the effective permeability. Elsewhere, we have shown that long-range correlations in the spatial distributions of diffusivity can induce memory effects and that these can be captured in the transient behavior of the effective permeability [20]. We argue that similar transient effects in the deviations from $k_0$ are responsible for the changes in effective transient permeability observed in the emulsion transport experiments. Hence, the parameters of the CTRW filtration such as the free state sticking rate $\Lambda$, may be correlated to the observed drops in permeability. If we consider that a drop in permeability affects the velocity of the carrying fluid
(the water), and that the dispersed phase moves advectively with the water, it is plausible to draw a connection between the retardation factor observed in the oil BTC experiments and the drop in permeability. Assuming that this working hypothesis holds, the corresponding drop in the permeability should be given by $k/k_0 \approx 1/R$. For the experimental results reported in figure 1 this corresponds to $k/k_0 = 0.63$, which is of the order of magnitude of permeability drops observed in literature for this kind of porous media (e.g., [2]). This conjecture can be tested in multiple-column laboratory experiments.

The relation of the $\beta$ exponent with the rheology of the emulsion remains poorly understood. Emulsion flow under simple experimental conditions exhibits non-Newtonian behavior such as aging and memory [21]. Further exploration is needed to test whether these non-Newtonian characteristics are also responsible for the memory effects observed in the more complicated geometries of porous media.

Finally, the importance of microscopic transitions in emulsion transport highlighted in this communication is likely to be important in other multiphase flow problems. Therefore, future research in multiphase flow theory need to address these effects in a self-consistent manner.

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