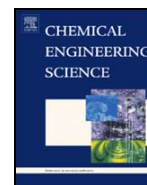




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Influence of miscible viscous fingering with negative log-mobility ratio on spreading of adsorbed analytes

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ABSTRACT

Viscous fingering (VF) between miscible fluids of different viscosities can affect the dispersion of localized samples in porous media. This is the case when a given fluid displaces a finite width sample consisting in a solvent of different viscosity and containing a dissolved analyte undergoing adsorption on the porous matrix. We investigate here numerically the influence of VF between the carrier fluid and the sample solvent on the spreading of a retained analyte concentration peak in a three-component system (displacing fluid, sample solvent, analyte). We compare the cases where the sample solvent is, respectively, more or less viscous than the displacing fluid or eluent by varying the log-mobility ratio $R = \ln(\mu_2/\mu_1)$ where μ_1 and μ_2 are the viscosities of the eluent and sample solvent, respectively. We show that disentanglement of the analyte concentration peak from the fingering zone occurs earlier for less viscous samples, i.e. for $R < 0$ than for $R > 0$. Qualitative agreement with experimental evidences obtained in reversed phase liquid chromatography are shown.

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1. Introduction

Whenever a fluid of a given viscosity displaces another more viscous miscible fluid in a porous medium, the interface between the fluids becomes unstable and deforms into a finger-like pattern. This interfacial hydrodynamic instability known as viscous fingering (VF) (Saffman and Taylor, 1958; Homsy, 1987) impacts many practical applications such as typically oil recovery in which the water displaces more viscous petroleum in underground reservoirs.

In applications like in chromatographic separations or in pollution events of aquifers where the contaminant zone is localized in space, fingering can occur if the sample is of different viscosity than the carrier fluid. This leads to an increased spreading of the sample in space and time. In chromatography, the resulting distortion of concentration peaks causes poor resolution in the separation of sample mixtures (Fernandez et al., 1996; Broyles et al., 1998; Dickson et al., 1997; De Wit et al., 2005; Rousseaux et al., 2007). The specificity of chromatography is that the sample injected into the column typically involves a mixture of analytes dissolved in a solvent which

can be more or less viscous than the eluent. Moreover adsorption of the analytes on the porous matrix usually takes place as well. A good modeling of fingering dynamics in chromatographic conditions should therefore ideally take into account at least three components: the sample solvent, the analyte and the displacing fluid. Moreover, the influence of adsorption of the analyte onto the porous matrix should be taken into account as well.

In this context, many experiments have been performed to evidence VF phenomena in a liquid chromatography column by considering different chemical components in the mobile phase and in the sample. Some examples are: sample and mobile phase of methanol-isopropanol system in different proportions (Cherrak et al., 1997), sample of uracil solutions and eluent of phosphate buffer in addition with glycerol (Czok et al., 1991), sample and mobile phase as a mixture of dichloromethane, toluene, and cyclohexanol in different proportions (Catchpole et al., 2006; Shalliker et al., 2007), etc. As a result, the viscosity of the sample μ_2 can either be smaller or larger than the viscosity μ_1 of the eluent. If the sample is less viscous, the log mobility ratio $R = \ln(\mu_2/\mu_1)$ is negative and fingering occurs at the frontal interface of the sample where the less viscous fluid pushes the more viscous carrier. On the contrary, when $R > 0$, fingering occurs at the rear front of the sample zone.

Theoretical studies of the specificities of VF of finite samples have been performed recently by De Wit et al. (2005) in the framework of chromatographic columns as well in pollution applications,

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by considering the displacement by a carrier fluid of a finite slice of another more viscous miscible fluid in a porous medium. The contribution of VF at the rear front of the sample has been characterized quantitatively and it has been shown that VF contributes transiently to the broadening of the peak in time by increasing its variance (Rousseaux et al., 2007). No analyte retention was considered in that case. In parallel, the differences between the distortion of peak shapes and its influence on the performance of the separation have been compared experimentally for $R > 0$ and < 0 by Czok et al. (1991), Cherrak et al. (1997) and Shalliker et al. (2007). In this regard, a theoretical quantitative comparison between fingering with positive and negative R without any adsorption has been discussed for finite samples by Mishra et al. (2008). It has been shown that the widening of the peaks is larger for negative R than for positive R . When $R < 0$ indeed, the propagation of viscous fingers occurs in the flow direction while VF develops in the opposite direction of the flow when $R > 0$.

The next step was to consider the role on VF of adsorption on the porous matrix as the adsorption of solutes dissolved in the sample can also influence the peak distortion. A series of experiments performed by Castells and Castells (1998) has studied dynamics for sample solvents whose viscosities were both larger or smaller than those of the mobile phase and the solutes were more or less retained. They have found that the distortion of the peaks increases as retention decreases. Recently, a two-component mathematical model has been developed by Mishra et al. (2007) to take into account such adsorption on the porous matrix of the species which rules the viscosity of the solvent. The nonlinear viscous fingering dynamics of finite length samples with effect of adsorption have been analyzed numerically. It was found that, when the species ruling the viscosity of the sample is retained, the fingering is similar to that of an unretained compound with a $(1 + k')$ smaller viscosity, where k' is the retention parameter.

However, in most practical chromatographic applications, it is not the solvent of the sample which is adsorbing on the porous matrix but rather the analytes dissolved in it. It is therefore important to consider a full three-component system where fingering develops between the eluent and the more or less viscous solvent of the sample in which analytes undergoing adsorption-desorption phenomena are dissolved. Relevant peak distortions in reversed phase liquid chromatography (RPLC) experiments have been reported by Castells and Castells (1998) and Keunchkarian et al. (2006), where VF develops at the unstable eluent and sample solvent interface and affects retained solute dynamics. Only the sample solvent concentration rules the viscosity of the miscible solution which is not influenced by the retained solute that acts as a passive scalar only. The solute band gets deformed by the convective motions within the fingers of sample solvent band, thus providing an indirect visualization of VF.

In order to model such situations, we have recently mathematically modeled miscible viscous fingering of a finite sample in a three component system consisting of the sample solvent, the eluent and a retained solute (Mishra et al., 2009). This first approach has focused on the case of positive R , i.e. the case when the sample solvent is more viscous than the eluent and fingering affects the rear interface of the sample. It has been shown that the distortions of the analyte peak is affected not only by viscosity difference between the sample solvent and the eluent but also by the retention parameter of the solute giving rise to different migration velocities of the solute and the solvent. The time of disentanglement between the solute and solvent spreading zones has been shown to occur later when fingering takes place than in the case of pure dispersion ($R = 0$).

However, in chromatography, for enhancing the solubility of the sample analytes, a sample solvent of a chemical nature or composition different from that of the eluent is sometimes selected. This sample solvent has most often a viscosity different from that of the

eluent and may be less viscous than the latter (Keunchkarian et al., 2006). In that case corresponding to $R < 0$, VF occurs at the frontal interface of the solvent band with a stable rear interface. In this context, the question is whether the disentanglement time between the solvent zone and the analyte one is different for $R > 0$ or $R < 0$ and to what extent it differs from a pure dispersive one. Although the stable rear front of the solvent zone acts as a barrier against the propagation of viscous fingers in the adsorption zone, does VF in the case of $R < 0$ nevertheless influence the displacement of a retained passive solute and how does the VF dynamics along or against the flow direction affect the transport of the passive analyte in the presence of adsorption?

To get a more quantitative insight into these questions, we undertake here a numerical comparative study of VF in a three component system when the log-mobility ratio R is respectively positive or negative which leads to VF of either the rear or frontal interface of the sample solvent band respectively. To do so, we use the model developed in Mishra et al. (2009) to consider the three components which are the displacing fluid, the sample solvent of different mobility and an analyte initially dissolved in the sample and undergoing adsorption-desorption on the porous matrix. The model couples Darcy's law for the evolution of the flow velocity to an equation describing the evolution of the concentration of the sample solvent and to a mass balance equation for the analyte concentration. Numerical simulations are performed with a viscosity-modifying solvent concentration and a passive retained analyte. Results are discussed in terms of the retention parameter k' for both positive and negative log-mobility ratios R . We find that the disentanglement of the analyte from the fingering of the solvent occurs much earlier for negative R than for positive R . Significant differences in the fingering patterns of the analyte plug are observed when varying the intensity of the log-mobility ratio R and the width l of the sample slice.

The article is organized as follows. We first summarize in Section 2 the three-component model with adsorption before presenting quantitative results in Section 3 and ending with conclusions.

2. Three component model with adsorption

We consider a two dimensional porous medium (or Hele-Shaw cell) of length L_x and width L_y (see Fig. 1) in which a sample of finite length W is injected at an initial time $t = 0$. The sample contains a solute or analyte in concentration $c_{a,2}$ dissolved in a solvent of viscosity μ_2 and concentration c_2 . This sample is displaced by the eluent, a miscible fluid of viscosity μ_1 in which the solute and sample solvent concentrations are $c_a = 0$ and $c = 0$, respectively. The eluent or carrier fluid is injected uniformly along the x direction with a mean velocity U .

The governing equations for an incompressible fluid flow inside the porous medium with the above three component system and dispersion can be written as (Mishra et al., 2009)

$$\nabla \cdot \underline{u} = 0, \quad (1)$$

$$\nabla p = -\frac{\mu(c)}{K_p} \underline{u}, \quad (2)$$

$$\frac{\partial c}{\partial t} + \underline{u} \cdot \nabla c = D_x \frac{\partial^2 c}{\partial x^2} + D_y \frac{\partial^2 c}{\partial y^2}, \quad (3)$$

$$\frac{\partial c_{a,m}}{\partial t} + F \frac{\partial c_{a,s}}{\partial t} + \underline{u} \cdot \nabla c_{a,m} = D_{ax} \frac{\partial^2 c_{a,m}}{\partial x^2} + D_{ay} \frac{\partial^2 c_{a,m}}{\partial y^2}, \quad (4)$$

where $\underline{u} = (u, v)$ is the 2D fluid velocity with u and v the velocity components in the x and y directions, respectively, K_p is the permeability of the porous medium and p is the pressure. Eqs. (1) and (2) are the continuity equation and Darcy's law, while Eq. (3) is the convection-dispersion equation for the concentration c of the solvent ruling the viscosity of the solution. Eq. (4) is the mass balance

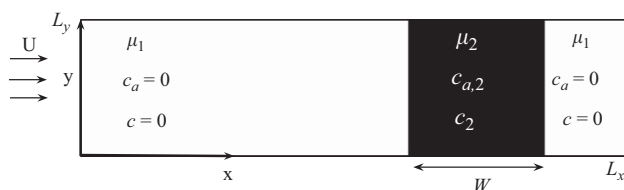


Fig. 1. Sketch of the system at initial time.

equation for the solute concentration c_a with a mobile and stationary phase concentration $c_{a,m}$ and $c_{a,s}$, respectively (Guiochon et al., 2006; Mishra et al., 2009). F is the phase ratio and D_x and D_y are the dispersion coefficients of the sample solvent in the displacing fluid along the x and y directions, respectively, while $D_{a,x}$ and $D_{a,y}$ are those of the analyte.

Here, assuming that the initial solute concentration $c_{a,2}$ in the sample solvent is small and does not influence the viscosity of the fluids, we consider the viscosity to be an exponential function of the solvent concentration c only such that

$$\mu(c) = \mu_1 e^{Rc/c_2}, \quad (5)$$

where the log-mobility ratio R is defined as $R = \ln(\mu_2/\mu_1)$. If $R < 0$, then $\mu_2 < \mu_1$ and the sample solvent is less viscous than the eluent. This gives rise to a stable rear interface while viscous fingering operates at the frontal interface (Mishra et al., 2008). If $R > 0$, then $\mu_2 > \mu_1$ and the opposite phenomenon occurs, i.e. the rear interface of the sample is unstable with regard to viscous fingering while the frontal interface is stable. The viscosity of the miscible solutions is not affected by the presence of the analyte which behaves as a passive scalar in the flow, but adsorption of this analyte on the porous matrix can nevertheless affect the spatio-temporal dynamics of its concentration. It is the goal of this paper to compare the effects of nonlinear fingering of the sample solvent on the dynamics of the analyte concentration with adsorption for $R > 0$ and < 0 .

We assume that the adsorption of the analyte onto the porous matrix follows a linear isotherm dependence between the concentration $c_{a,s}$ and $c_{a,m}$, i.e. $c_{a,s} = Kc_{a,m}$, with K the adsorption-desorption equilibrium constant. Eq. (4) becomes therefore

$$(1 + k') \frac{\partial c_{a,m}}{\partial t} + \underline{u} \cdot \nabla c_{a,m} = D_{a,x} \frac{\partial^2 c_{a,m}}{\partial x^2} + D_{a,y} \frac{\partial^2 c_{a,m}}{\partial y^2}, \quad (6)$$

where $k' = FK$ is the retention factor.

We non-dimensionalize the governing equations by using c_2 and $c_{a,2}/(1 + k')$ as the reference concentration for the solvent and solute concentrations, respectively, U as the characteristic velocity, a length scale $L_c = D_x/U$ and a time scale $t_c = D_x/U^2$. The analyte concentration $c_{a,m}$ in the mobile phase is scaled with the mobile phase concentration of the analyte in the sample $c_{a,2,m} = c_{a,2}/(1 + k')$, for a detailed derivation see Mishra et al. (2009). Using a frame of reference moving with speed U and introducing the stream function $\psi(x, y)$, such that $u = \partial\psi/\partial y$ and $v = -\partial\psi/\partial x$, the governing Eqs. (1)–(3) and (6) with the concentration-dependent viscosity Eq. (5) become in dimensionless variables (Mishra et al., 2009),

$$\nabla^2 \psi = -R \left(\frac{\partial \psi}{\partial x} \frac{\partial c}{\partial x} + \frac{\partial \psi}{\partial y} \frac{\partial c}{\partial y} + \frac{\partial c}{\partial y} \right), \quad (7)$$

$$\frac{\partial c}{\partial t} + \frac{\partial \psi}{\partial y} \frac{\partial c}{\partial x} - \frac{\partial \psi}{\partial x} \frac{\partial c}{\partial y} = \frac{\partial^2 c}{\partial x^2} + \varepsilon \frac{\partial^2 c}{\partial y^2}, \quad (8)$$

$$(1 + k') \frac{\partial c_{a,m}}{\partial t} + \left(\frac{\partial \psi}{\partial y} - k' \right) \frac{\partial c_{a,m}}{\partial x} - \frac{\partial \psi}{\partial x} \frac{\partial c_{a,m}}{\partial y} = \delta \left[\frac{\partial^2 c_{a,m}}{\partial x^2} + \varepsilon_a \frac{\partial^2 c_{a,m}}{\partial y^2} \right], \quad (9)$$

where $\varepsilon = D_y/D_x$, $\varepsilon_a = D_{a,y}/D_{a,x}$ and $\delta = D_{a,x}/D_x$ are the dispersion ratios. From the above equations it is clear that Eq. (9) is decoupled from Eqs. (7) and (8). Hence, once the stream function is determined from Eqs. (7) and (8) for given R and ε , the transport of the solute concentration $c_{a,m}$ can be analyzed easily for different values of the analyte parameters ($k', \delta, \varepsilon_a$). The objective here is to analyze how the dynamics of the sample solvent and of the passive analyte can disentangle depending on the intensity of adsorption.

Eqs. (7)–(9) are numerically solved using the pseudo-spectral method introduced by Tan and Homsy (1988) which has been tested for convergence (Mishra et al., 2009). It is based on a predictor-corrector method to solve the time dependent equation obtained with a Fourier expansion. Boundary conditions are periodic in both x and y directions. In non-dimensional units, the length and width are respectively $L = UL_x/D_x$ and $L' = UL_y/D_x$ while the non-dimensional initial length of the sample is $l = UW/D_x$. The initial conditions for both the concentration c and $c_{a,m}$ correspond to a rectangular sample of concentration $c = c_{a,m} = 1$ and of size $L' \times l$ in a $c = c_{a,m} = 0$ background. They can be expressed as, $c = c_{a,m} = H(x - x_0 + l/2) - H(x - x_0 - l/2)$, where $x_0 \in [l/2, L - l/2]$ is the middle of the sample, with an intermediate point $c = c_{a,m} = 1/2 + Ar$ at the jump discontinuities between 0 and 1. Here r is a random number between 0 and 1 and A is the amplitude of the noise of the order 10^{-3} which is used to induce the fingering instability on a pertinent computing time (De Wit et al., 2005).

3. Viscous fingering effects on the analyte displacement

The aim of the present study is first to analyze the dynamics of the analyte displacement for a negative log-mobility ratio R , i.e. when viscous fingering occurs at the frontal interface of the sample where the less viscous sample solvent displaces the eluent. We next compare it with the case $R > 0$ for the same viscosity ratio when VF occurs at the rear interface. In order to visualize such dynamics, the concentration field $c_{a,m}$ is followed in Fig. 2 for different values of the retention parameter k' in a frame of reference moving with the dimensionless constant speed of the unperturbed sample. On a gray scale from black to white corresponding to $c_{a,m} = 1$ and $c_{a,m} = 0$, respectively, (on color blue and red correspond to $c_{a,m} = 1$ and 0, respectively) and the figures are presented with a constant aspect ratio. In the absence of adsorption, $k' = 0$ and the analyte acts as a passive scalar following the same fingering dynamics as that of the sample solvent (see Fig. 2(a)). For $R < 0$ this fingering occurs at the frontal interface of the analyte plug whereas the rear interface is stable. In the presence of adsorption onto the porous matrix the dynamics of the analyte becomes however different from that of the solvent as shown in Fig. 2(b)–(d) for different values of the retention parameter $k' > 0$. The VF dynamics of the solvent affects the evolution of the analyte concentration $c_{a,m}$ as it deforms its concentration field because of the convection motions. For a fixed time, it is only at larger values of k' that the retained analyte plug disengages from the sample solvent plug showing then a dispersive displacement only, without any distortion of the peak. For example, at time $t = 7000$, the frontal interface of the analyte zone for $k' = 0.2, 0.3$ (see Fig. 2(b) and (c)) are unstable showing the distortion due to the VF of sample solvent while both interfaces of the analyte plug are stable for $k' = 0.4$ (see Fig. 2(d)). Note that the rear interface of the analyte zone is always stable for $R < 0$ and only the frontal interface shows the distortion because that interface only comes into contact with the unstable interface of the sample solvent VF. However for the case $R > 0$ both interfaces of the analyte plug can become unstable as they both come in contact with the sample solvent VF during the displacement (Mishra et al., 2009).

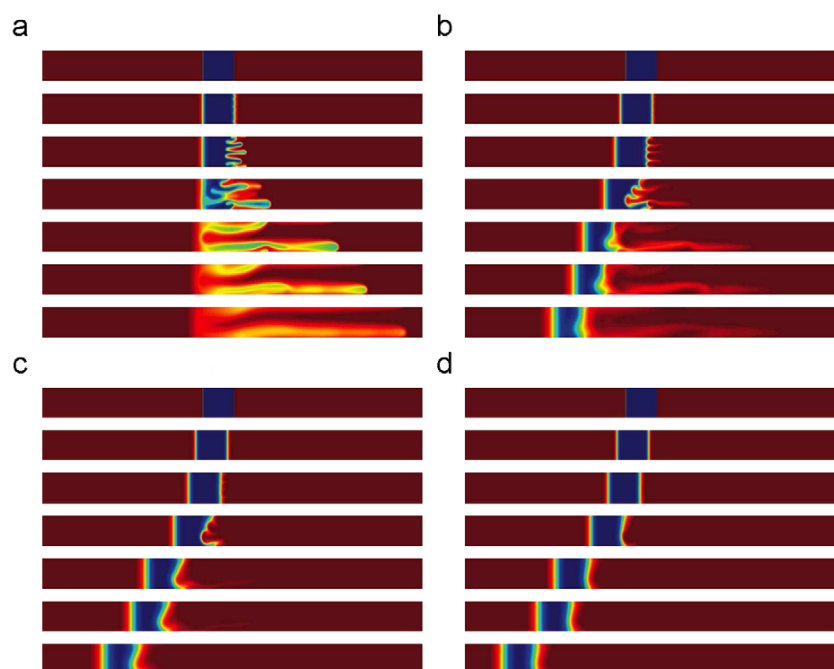


Fig. 2. (color online) Evolution of the concentration $c_{a,m}$ in a reference frame moving with the injection velocity with $L' = 512, \varepsilon = 1, \varepsilon_0 = 1, \delta = 1, l = 512, R = -2$; (a) $k' = 0$, same dynamics as that of the sample solvent concentration, (b) $k' = 0.2$, (c) $k' = 0.3$, (d) $k' = 0.4$. From top to bottom in (a–d): $t = 0, 500, 1000, 2000, 4000, 5000, 7000$.

3.1. Transversely averaged concentration profiles

In order to compare the results for both $R > 0$ (Mishra et al., 2009) and $R < 0$ quantitatively, we analyze transversely averaged concentration profiles defined as (De Wit et al., 2005; Mishra et al., 2007, 2008)

$$\bar{c}_{a,m}(x,t) = \frac{1}{L'} \int_0^{L'} c_{a,m}(x,y,t) dy. \quad (10)$$

Such profiles give insight into peak measurements as would be done by detectors placed along a chromatographic column (Bacri et al., 1991). Fig. 3(a) depicts $\bar{c}_{a,m}(x,t)$ at $t = 5000$ for the simulations of Fig. 2 with $R = -2$ while simulations with $R = 2$ are shown in Fig. 3(b). The dotted line shows the averaged profile of the injected sample at $t = 0$, its center being repositioned at $x = 0$. In the case $R = -2$ (Fig. 3(a)), the corresponding non-adsorptive curve ($k' = 0$) shows the characteristic distortions and broadening at the frontal interface sample solvent peak due to VF as discussed in Mishra et al. (2008). Similar dynamics are observed at the rear interface for $R = 2$ (Fig. 3(b)). In the presence of adsorption ($k' \neq 0$), the analyte travels towards the left (upstream flow) with regard to the sample solvent zone for both $R > 0$ and < 0 . For small retention parameters ($k' = 0.2, 0.3, 0.4$) with positive log mobility ratio both rear and frontal interfaces get distorted (Fig. 3(b)), while with negative log mobility ratio only the frontal interface shows the bumps (Fig. 3(a)) when the retention parameter $k' = 0.2, 0.3$. For $k' = 0.4$ and $R < 0$, the analyte zone completely disengages from the sample solvent zone with non-deformed rear and frontal interfaces. The interesting observation is that the length of the analyte spreading zone is larger for $R = -2$ than for $R = 2$, as seen from comparing the dashed and dash-dotted curves corresponding to $k' = 0.2$ and 0.3 , respectively. It is due to the fact that the analyte gets spread along the fingering front of the sample solvent as long as the analyte zone is in contact with the VF zone. The spreading length of the analyte peak is larger for $R < 0$ than for

$R > 0$ as there is more spreading of VF along the flow direction than for VF in the opposite direction of the flow.

As in Mishra et al. (2009), this spreading length is quantified by the length of the interval L_d in which $\bar{c}_{a,m}(x,t) > 10^{-3}$. The evolution of L_d , corrected by a factor $\sqrt{2\delta/(1+k')}$, is furthermore depicted in Fig. 4 for different k' values. This correction factor is introduced to eliminate the k' -dependence appearing in a purely dispersive case since, in the latter, the standard deviation of the analyte concentration evolves as $\sqrt{2\delta t/(1+k')}$. It is clearly observed that the spreading of the analyte evolves at early times proportionally to \sqrt{t} (the characteristic slope of pure dispersion) for all k' . Furthermore when VF interacts with the analyte distribution in the case $k' = 0$ or small k' ($k' = 0.2, 0.3$), the spreading length deviates from that value with a slope $\frac{1}{2}$. For $k' = 0.2$, the deformation is even larger than for $k' = 0$ because the retardation zone due to adsorption adds to that due to fingering. But for $k' = 0.4$ the analyte is affected by VF for some times and then disentangles from the sample solvent plug showing a further evolution as \sqrt{t} . The time interval of the interaction between the analyte and the sample solvent reduces when k' increases. It can be seen that the dashed line corresponding to $k' = 0.5$ in Fig. 4 has a very small interval of deviation before approaching the line with slope \sqrt{t} and there is no deviation for further larger values as $k' = 1$ for example. Here, we note that the power-law relationship of the dispersion length of the analyte after being affected by VF follows the same power $\frac{1}{2}$ as in the case without VF, however this power-law relationship is observed to be smaller than $\frac{1}{2}$ in the case $R = 2$ (Mishra et al., 2009).

3.2. Effects of VF on standard deviation of $\bar{c}_{a,m}(x,t)$

In order to quantify the peak broadening of the mobile phase concentration of the analyte $\bar{c}_{a,m}(x,t)$, similarly to previously quantified results in the literature (De Wit et al., 2005; Mishra et al., 2007, 2008), the standard deviation $\sigma_a(t)$ of $\bar{c}_{a,m}(x,t)$ is computed using the

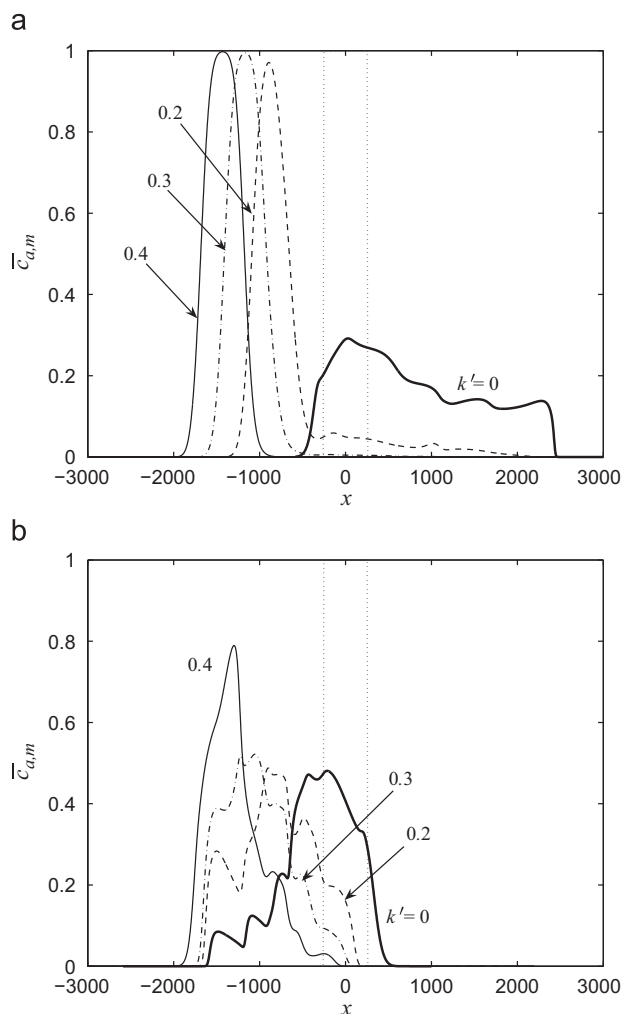


Fig. 3. Transversely averaged concentration profiles $\bar{c}_{a,m}$ at $t = 5000$ for different values of k' and simulations of Fig. 2 for (a) $R = -2$ and (b) $R = 2$. The dotted line is the initial position of the sample.

definitions of central normalized moments and defined as:

$$\sigma_{af}(t) = \sqrt{\frac{\int_0^L \bar{c}_{a,m}(x,t)[x - m(t)]^2 dx}{\int_0^L \bar{c}_{a,m}(x,t) dx}} \quad (11)$$

where $m(t) = \frac{\int_0^L x f(x,t) dx}{\int_0^L f(x,t) dx}$ is the first moment of $f(x,t) = \bar{c}_{a,m}(x,t) / \int_0^L \bar{c}_{a,m}(x,t) dx$. Like previous studies of VF of finite slices, we can extract the quantity σ_{af} defined as

$$\sigma_{af} = \sqrt{\sigma_a^2 - \sigma_{a,0}^2}$$

where

$$\sigma_{a,0}^2 = \frac{l^2}{12} + \frac{2\delta t}{1+k'}$$

is the variance of a pure dispersive analyte distribution when $R = 0$. The term $l^2/12$ corresponds to the contribution due to the initial width l of the sample, while the linear term in t is due to dispersive mixing. The quantity σ_{af} is a standard deviation contribution of viscous fingering to the analyte variance σ_a^2 .

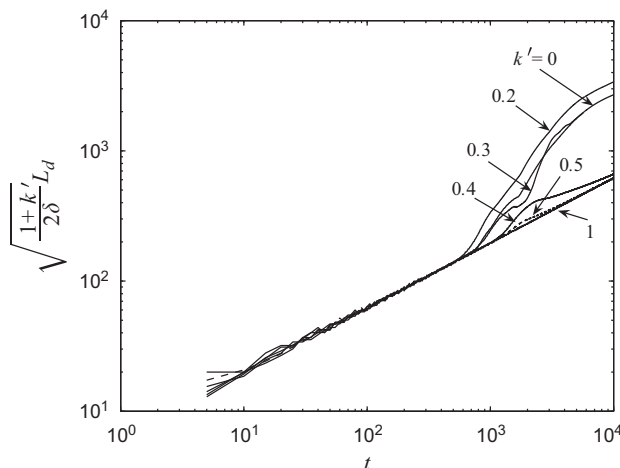


Fig. 4. Log-log plot of the normalized spreading length of the analyte as a function of time for different values of k' for the simulations of Fig. 2.

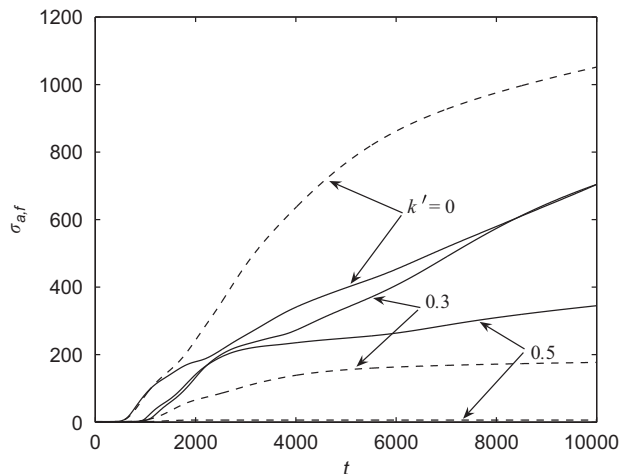


Fig. 5. Temporal evolution of σ_{af} for $R = 2$ (solid lines) and $R = -2$ (dashed lines) for various values of k' and $L' = 512, \epsilon = 1, \epsilon_a = 1, \delta = 1, l = 512$.

Fig. 5 compares the quantity σ_{af} for both positive and negative log mobility ratios for various values of the adsorption parameter k' . We know from De Wit et al. (2005) and Mishra et al. (2009) that σ_{af} starts to deviate from zero at the onset of VF effects on the analyte distribution and next increases with time when VF is effective then eventually saturates to an asymptotic value when VF dies out and dispersion takes over. This asymptotic dispersive regime also occurs when the analyte plug completely disengages from the sample solvent plug. For the non-adsorptive case $k' = 0$, σ_{af} is larger when $R = -2$ than when $R = 2$. This comes from the fact that the influence of VF between the solvent and the eluent is larger when VF arises in the flow direction ($R < 0$) than against the flow ($R > 0$). However, in the presence of adsorption ($k' \neq 0$) the effects of VF on the analyte broadening is smaller for $R < 0$ than for $R > 0$ as seen on Fig. 5 showing that, for $k' = 0.3, 0.5$, the standard deviation σ_{af} is lower and saturating to a constant value earlier for $R = -2$ than for $R = 2$.

For the case of pure dispersion, $R = 0$, the critical time of disengagement of the analyte and of the solvent plug can be obtained

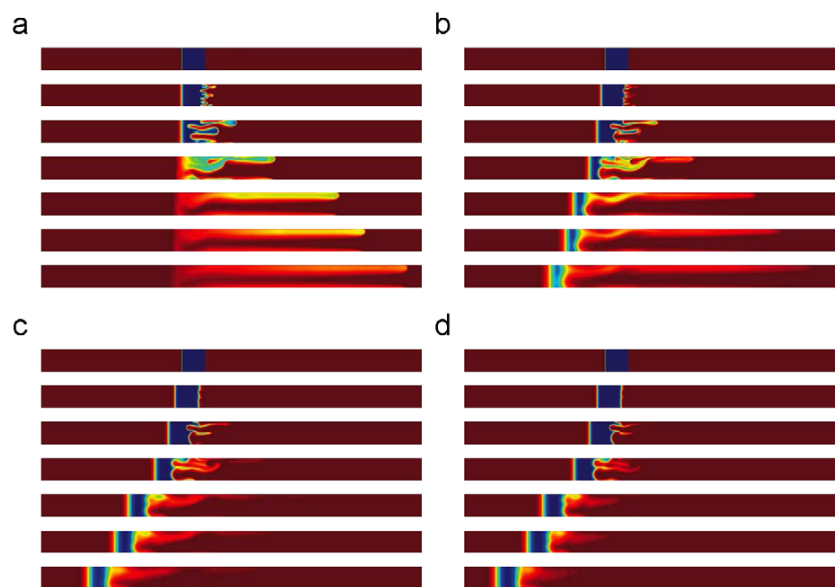


Fig. 6. (color online) Same as Fig. 2 for $R = -3$ and (a) $k' = 0$, (b) $k' = 0.2$, (c) $k' = 0.4$ and (d) $k' = 0.5$.

mathematically by looking for the time when the rear interface of the solvent is ahead of the frontal interface of the analyte. By equating the positions of those interfaces, we get the critical time t_{crit} as Mishra et al. (2009)

$$t_{crit} = \left(\frac{1+k'}{k'}\right)^2 \left[\sqrt{2} \left(1 + \sqrt{\frac{\delta}{1+k'}}\right) + \sqrt{2 \left(1 + \sqrt{\frac{\delta}{1+k'}}\right)^2 + \frac{k'}{1+k'} l} \right] \quad (12)$$

It may look obvious that the disengagement of the sample solvent and of the analyte plug may occur for $R < 0$ at the same time as for pure dispersion ($R = 0$) since VF is seen only at the frontal front of the solvent while the stable rear front does not then affect the analyte distribution as it travels towards the left of the solvent zone. However, it does not happen in the presence of nonlinear dynamics because the nonlinear VF which occurs at the frontal front delays the disentanglement of the analyte zone from the sample solvent zone. It is clear from the results for $R = -2$ and $k' = 0.3$, shown in Figs. 2 and 5, that the disentanglement occurs at a time close to $t = 6000$ instead of $t = 3600$ for the corresponding pure dispersive case $R = 0$ found from Eq. (12) by fixing the parameters $\delta = 1, l = 512$. Fig. 5 also shows that the onset time of solute fingers by VF for a given adsorption constant is the same for both $R > 0$ and < 0 .

3.3. Parametric study

In the case of liquid chromatography (Catchpoole et al., 2006; Shalliker et al., 2007), the log-mobility ratios R can be varied by choosing different compositions and viscosities of eluent and sample solvent liquids. It is well known that the larger the value of R , the more intense VF is observed (Cherrak et al., 1997; De Wit et al., 2005; Mishra et al., 2008). In order to see the effects of R for a less viscous sample solvent, the concentration $c_{a,m}$ for $R = -3$ are plotted in Fig. 6 for different values of the retention parameter k' in order to compare with the $R = -2$ case of Fig. 2. It is observed that, for any

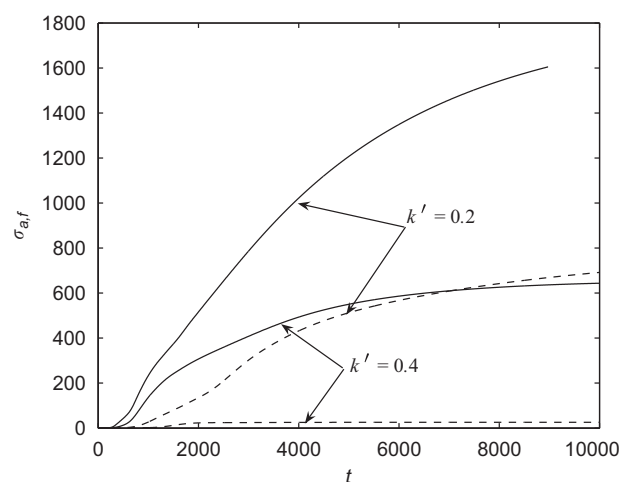


Fig. 7. Influence of k' on the temporal evolution of σ_{af} with $R = -3$ (solid lines) and $R = -2$ (dashed lines) and $L' = 512, \varepsilon = 1, \varepsilon_a = 1, \delta = 1, l = 512$.

fixed value of k' , the spreading length of the analyte in the case of $R = -3$ is larger than for $R = -2$.

In Fig. 7 we have plotted the quantity σ_{af} for two different values of $R < 0$. It is seen that the asymptotic diffusive regime is reached earlier for $R = -2$ than $R = -3$. For $k' = 0.4$, this asymptotic saturation is already achieved at around $t = 3000$ in the case of $R = -2$ (see Figs. 2(d) and 7), while it is not yet achieved for $R = -3$ (see Figs. 6(c) and 7). Hence the larger the intensity of VF the larger the delay in the disengagement of the analyte plug from the solvent plug even with a stable rear interface of the solvent plug. Similarly the smaller the dispersion ratio ε and the larger L' the more intense VF is (De Wit et al., 2005) and hence the larger the delay in the disengagement between the analyte and the less viscous sample solvent zone.

The influence of the width l of the sample on the broadening of the analyte in the presence of the less viscous sample solvent

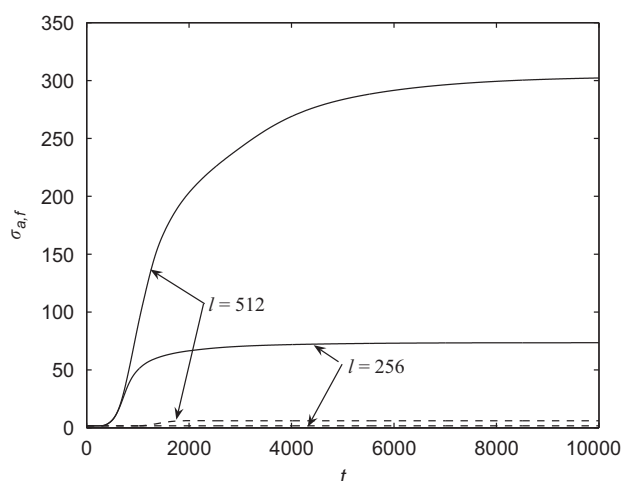


Fig. 8. Influence of l on the temporal evolution of $\sigma_{a,f}$ with $R = -3$ (solid lines) and $R = -2$ (dashed lines) and $L' = 512$, $\varepsilon = 1$, $\varepsilon_a = 1$, $\delta = 1$, $k' = 0.5$.

VF are shown in Fig. 8. The larger the length of the sample, the larger the mixing zone between the sample solvent and eluent, hence VF influences on a longer time the analyte zone showing that the quantity $\sigma_{a,f}$ is larger for increasing l . The asymptotic diffusive regime of the analyte concentration is reached later for $l = 512$ than for $l = 256$ and also later for $R = -3$ than for $R = -2$ as discussed above.

4. Conclusion

In liquid chromatography or localized soil contamination problems the sample fluid viscosity can be different from that of the carrier fluid. This can cause the broadening of the sample due to fingering patterns arising from the viscosity mismatch between both fluids. The adsorption onto the porous matrix of a solute or analyte transported as a passive scalar by the sample solvent can moreover affect the peak evolution of the analyte. Such peak dynamics is analyzed here in both cases of sample solvents more or less viscous than the eluent in a three component system: the analyte, the solvent and the carrier fluid. The disentanglement between the analyte and sample solvent zones occurs earlier for negative log mobility ratio R (less viscous solvent) than for positive R (more viscous solvent). Such disentanglement occurs later for negative R than for pure dispersion ($R = 0$) in spite of the stable rear interface of the sample solvent zone in $R < 0$, as the analyte peaks are distorted due to the unstable frontal interface of the sample solvent. These differences in the dynamics of analyte concentration for both positive and negative R are reported in RPLC experiments (Castells and Castells, 1998; Keunchkarian et al., 2006) and are in good agreement with our above results.

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