ABSTRACT: We have studied the chromatographic separation of solvents and dyes after deposition of a dye solution on a paper substrate. Due to their larger molecular size, dyes typically exhibit a stronger interaction with the paper constituents. Consequently, the imbibition process of the dye is usually delayed compared to that of the solvent. This impacts the achievable resolution and color homogeneity in inkjet printing. We present experiments and a comprehensive numerical model to illustrate and quantify these effects. The model accounts for the solvent evaporation, heat transfer, multicomponent unsaturated flow, and dye adsorption, as well as the presence of permeable fibers in the paper substrate. We identify the key parameters that can be tuned to optimize the pattern fidelity of the printing process.

INTRODUCTION

Chromatography is an analytical technique employed for the separation of a multicomponent liquid or gaseous sample during flow through a polymeric or porous matrix based on the different molecular interactions of the individual components with the host matrix.1 The individual components move at smaller average speeds than the solvent and accumulate into bands or peaks. The shape of the peaks and the speed of propagation contain information on specific interactions. In thin-layer chromatography, paper substrates are frequently used.2,3 In the corresponding paper-based microfluidic devices, the flow mechanism is usually based on spontaneous capillary imbibition.4,5

Printing inks are typically multicomponent solutions of colorants, surfactants, humectants, and numerous other additives in aqueous or organic solvents.6 Upon contact with paper, capillary imbibition causes the flow of the solution. While progressive absorption of the solvent into the paper is usually desirable, it is generally undesirable if the ink colorants are transported significant distances from the ink deposition zone, as this diminishes the achievable resolution of the printing process. Similarly undesirable is the chromatographic separation of dye mixtures or non-homogeneous dye concentration profiles because these degrade the color uniformity and contribute to edge mottling.

Donigian et al. studied the chromatographic retention of dyes on thin coating layers frequently used as top coats on high-quality paper types optimized for inkjet printing.7 They studied the effect of the binder concentration on coatings containing either silica or calcium carbonate nanoparticltes. Sodhi et al. and Filenkova et al. applied secondary ion mass spectrometry to characterize the spatial distributions of various ink components after inkjet printing of a long line with an approximate width of 200 μm.8,9 For a coated paper, the line width is homogeneous, whereas for an uncoated paper, the line edges are ragged. In both cases, however, the dye front clearly lags behind the ink vehicle front.

Lamminmäki et al. studied the chromatographic separation of an anionic dye in thin porous layers composed of porous CaCO₃ microparticles and either anionic or cationic binders.10 These materials are commonly used as coating top layers in photo-quality papers optimized for inkjet printing. The porous layer was oriented vertically and dipped into a horizontal reservoir filled with an aqueous solution of an anionic dye. Depending on whether the charges of the dye and the host matrix were of equal or opposite polarity, the retention of the dye molecules was either weak or very strong during the propagation of the water front up the porous layer.

The purpose of this paper is to present a numerical model for the imbibition and evaporation of a dye-based model ink containing a molecularly dissolved colorant in a solvent into and from paper substrates. The presence of fibers in the paper substrate is explicitly taken into account. The dye–paper interaction is described by the Langmuir-type rate equation for adsorption and desorption. The numerical simulations are complemented by experiments using anionic and cationic fluorescent dyes deposited either by drop-casting or inkjet printing.

MATERIALS AND METHODS

The paper type we used was Mondi DNS HSI NF with a thickness t_p = 104 μm, which contains CaCl₂ to aid the inkjet print quality. We used two different fluorescent dyes: the cationic red dye Rhodamine B

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moving the paper substrate laterally with a speed than being in contact with a solid surface. In the inkjet setup, the surface, that is, both sides of the paper are surrounded by air rather cases, the paper substrates are mounted about 6 mm above a solid surface. When the deposited ink quantity exceeds the maximum holding capacity \( \Theta_{\text{max},\text{hold}} \approx 94 \text{ g/m}^2 \) of the paper substrate, the moisture content and the dye concentration will quickly equilibrate throughout the thickness direction of the paper sheet and subsequently spread along its lateral dimension in a quasi-1D fashion. This allows us to use microscopy as a non-destructive method for measuring the chromatographic separation of solvent and dye in a time-resolved fashion over large distances compared to the paper thickness. In commercial inkjet printing, the penetration depth of the colorant front is much smaller than the thickness of a paper sheet,\textsuperscript{12} such that both lateral and vertical transport must be considered. However, the governing physical mechanisms are identical.

### THEORETICAL MODEL

Murali \textit{et al.} and Venditti \textit{et al.} developed a theoretical model for the in plane transport of moisture, surface-active solutes, and heat in thin, fibrous, and moving porous media.\textsuperscript{11,13} They assumed that at time \( t = 0 \), the transport and equilibration of moisture and colorant in the thickness direction were already complete. We adopted this model to describe the absorption and evaporation of an inkjet ink consisting of a non-surface-active colorant that is molecularly dissolved in a solvent after deposition onto a stationary horizontal sheet of paper. Below, we only list the main dynamic equations; for further details, the readers are referred to refs\textsuperscript{11,13}.

We use a Cartesian coordinate system with the \( x \)-axis parallel to the printing direction. The vertical \( z \)-axis is perpendicular to the horizontal paper sheet.

The model explicitly accounts for the presence of permeable fibers by means of a dual-porosity description. The moisture content \( \Theta_f \) inside the fibers is assumed immobile.\textsuperscript{14} Consequently, the dynamic equation for \( \Theta_f \) (units kg/m\(^2\)) contains only flux terms but no transport terms

\[
\frac{\partial \Theta_f}{\partial t} = j_{\text{tr},f} - j_{\text{ev},f} \tag{3}
\]
Here, \( s_{\text{ad}} \) is the pore–fiber moisture exchange rate and \( j_{\text{ev, f}} \) the evaporative flux from the fibers to the ambient atmosphere. The time evolution of the pore moisture content \( \Theta_w \) is governed by the Richards equation,\(^{15}\) integrated along the thickness direction of the paper substrate\(^{11}\)

\[
\frac{\partial \Theta_w}{\partial t} - \frac{\rho_w}{\mu_w} V_{2D}(t, K_w V_{2D} P_w) = - j_{\text{ev, w}} - s_{\text{pf}}
\]

(4)

where \( \rho_w \) and \( \mu_w \) are the mass density and viscosity of the ink, respectively, \( t_p \) is the permeability of the paper, \( K_w \) is the permeability, \( P_w \) is the capillary pressure, \( j_{\text{ev, w}} \) is the evaporative flux from the pores to the ambient atmosphere, and \( V_{2D} \equiv (\partial / \partial x, \partial / \partial y) \). We assume that \( K_w \) is unaffected by the presence of the colorant. Moreover, we assume that the ink viscosity increases with dye concentration according to the empirical relation

\[
\mu(c) = \mu_{H_2O} \exp(c / c_1)
\]

(5)

where \( c_1 = 51.4 \text{ kg/m}^3 \). Equation 5 corresponds to the material properties of aqueous solutions of Triton X-100 and is chosen merely such that the generic behavior. The evaporation process is assumed to be diffusion-limited. The total evaporative flux \( j_{\text{ev}} \) is given by

\[
j_{\text{ev}} \equiv j_{\text{ev, w}} + j_{\text{ev, f}} = k_{\text{a}}(\rho_i - \rho_{\text{amb}})
\]

(6)

where \( \rho_i \) is the water vapor concentration at the paper surface, \( \rho_{\text{amb}} \) is the ambient water vapor concentration, and \( k_{\text{a}} \) is a mass-transfer coefficient.

The total moisture content is defined as \( \Theta_{\text{tot}} \equiv \Theta_w + \Theta_f \). Its value for paper in equilibrium with ambient conditions is denoted \( \Theta_{\text{amb}} \). In the following, we shall also be referring to the dimensionless total moisture content defined as \( \tilde{\Theta}_{\text{ad}} \equiv \Theta_{\text{tot}} / \Theta_f \) where \( \Theta_f \approx 77 \text{ g/m}^2 \) is the mass density of a dry paper. The maximum water holding capacity of the paper substrate is denoted \( \Theta_{\text{max}} \). Its dimensionless variant is \( \tilde{\Theta}_{\text{max}} \) which is assumed to have a value of \(^{13}\) 1.5.

The heat transfer equation is given by\(^{11}\)

\[
\frac{(\rho c_p)_{aw}}{\partial T} + \rho_i c_{p,i} \bar{V}_{2D} V_{2D} T = \frac{q'_{2D}}{t_p} + \Phi_i + V_{2D} \cdot (k_w V_{2D} T)
\]

(7)

where \( T \) is the temperature, \( c_{p,i} \) the specific heat capacity of the ink, \( \Phi_i \) is the heat of sorption, \( \bar{V}_{2D} \equiv -(K_w/\mu_w) V_{2D} P_w \) represents the in-plane components of the Darcy velocity, and \( k_w \) and \( (\rho c_p)_{aw} \) are the averaged thermal properties of wet paper. Moreover

\[
q'_{2D} \equiv h_{\text{aw}}(T - T_{\text{amb}}) - j_{\text{ev}} E_{\text{ev}}
\]

(8)

is the heat flux accounting for the heat exchange with the ambient environment and evaporative cooling. Here, \( h_{\text{aw}} = 9 \text{ W/(m}^2\text{K)} \) is the heat-transfer coefficient, \( T_{\text{amb}} \) is the ambient temperature, and \( E_{\text{ev}} = 2.45 \text{ MJ/kg} \) is the enthalpy of evaporation of water. The transport of the colorant is governed by the following set of equations

\[
\frac{\partial}{\partial t} (c \Theta_w) + \rho_w V_{2D} (t_p \bar{V}_{2D})c = V_{2D} (\Theta_w D_{2D} V_{2D} c) - c_{pf} - s_{ad} \Theta_w
\]

(9)

\[
\frac{\partial}{\partial t} (c_{ad}) = c_{pf}
\]

(10)

\[
\frac{\partial C_{ad}}{\partial t} = s_{ad}
\]

(11)

Here, \( c \) and \( c_{ad} \) are the colorant concentrations (units kg of dye per cubic meter of ink) in the pores and fibers, respectively, and \( C_{ad} \) is the adsorbed colorant concentration (units kg of dye per kg of paper). The term \( \Theta_{2D} D_{2D} V_{2D} c \) in eq 9 accounts for the diffusion and dispersion of the colorant. The dye in the fibers is assumed to be immobile. The term \( c_{pf} \) represents the pore–fiber exchange rate. There is no evaporative solute flux term because the colorant is assumed to be non-volatile. Evaporation-induced concentration increases are, however, accounted for, as a decrease in \( \Theta_w \) automatically leads to a proportional increase in \( c \). The right-hand side of eq 11 is the adsorptive flux

\[
s_{ad} \equiv k_{ad} \left[ 1 - \frac{C_{ad}}{C_{\text{inf}}} \right] - k_{de} \frac{C_{ad}}{C_{\text{inf}}}
\]

(12)

which corresponds to the Langmuir adsorption isotherm\(^{16}\) with adsorption and desorption rate constants \( k_{ad} \) and \( k_{de} \) respectively, and sorption capacity \( C_{\text{inf}} \). The parameter \( C_{\text{inf}} = 0.15 \text{ kg/m}^3 \) is introduced merely such that \( k_{ad} \) and \( k_{de} \) have the same dimensions. The adsorption process described by eq 12 is completely reversible, that is, flushing with pure water will eventually desorb the colorant completely.

**Boundary Conditions and Initial Conditions.** We performed one- (1D) and two-dimensional (2D) numerical simulations using the computational domains in Figure 2a,b.

![Figure 2. Sketch of the computational domains for the (a) 1D and (b) 2D simulations.](https://doi.org/10.1021/acs.langmuir.1c01624)

The corresponding initial conditions (ICs) are depicted as the blue curve in Figure 2a and the red distribution in Figure 2b. At time \( t = 0 \), we assume that imbibition of the ink in the thickness direction of the paper is already complete and that no ink is left on top of the paper. The water fronts and colorant fronts still coincide, that is, we assume that no adsorption has occurred, yet. Moreover, we assume that the water in the pores is in capillary equilibrium with the water in the fibers.

The blue curve in Figure 2a corresponds to the cross section of a printed line, as depicted in Figure 1e. The computational domain extends from the center of the printed line \( y = 0 \) to \( y = L \), where \( L \) is chosen sufficiently large such that the water front never reaches the right boundary prior to complete evaporation. Consequently, the boundary conditions (BCs) at \( y = 0 \) correspond to mirror symmetry or no-flux conditions, that is, the y-derivatives of all quantities vanish there.
\[
\frac{dc}{dy} = 0 = \frac{\partial C_d}{\partial y} = \frac{\partial \theta_w}{\partial y} = \frac{\partial \theta_l}{\partial y} = \frac{\partial T}{\partial y}
\]  
(13)

At the right boundary \( y = L \), all quantities take their ambient values far away from the deposition zone, that is

\[
c = 0 \Rightarrow c_l = C_{ad}, \quad \theta_w = \theta_{w, amb}, \quad T = T_{amb}
\]  
(14)

The 2D simulations consider the line formation in inkjet printing, that is, the deposition of a 1D array of individual droplets that will eventually merge. The individual droplets give rise to a periodic moisture distribution of period \( \Delta x_{\text{drop}} = 2 \pi R_\text{drop} \), where each period consists of a circular segment of radius \( R_\text{drop} \). Typically, inkjet droplets are printed with a non-zero overlap, that is, the value of \( \alpha \) is smaller than 1. Due to the inherent symmetries, the computational domain needs to span only half a period in the \( x \)-direction, as indicated by the black rectangle in Figure 2b. The corresponding BCs on the boundaries labeled \( \odot \), \( \odot \), and \( \odot \) correspond to no-flux conditions as

\[
\vec{n} \cdot \nabla c = 0 = \vec{n} \cdot \nabla \theta_w = \vec{n} \cdot \nabla \theta_l = \vec{n} \cdot \nabla T
\]  
(15)

where \( \vec{n} \) is a 2D unit normal vector defined at the boundaries of the computational domain. The height of the rectangle is sufficiently large such that the water front never reaches it. Consequently, the BCs on boundary \( \odot \) are given by eq 14. At \( t = 0 \), the positions of the water front and the colorant front are assumed to coincide [black solid line in Figure 2b].

**Scales and Dimensionless Parameters. Concentration.**

The colorant concentration \( c \) of the ink is expressed in mass per unit volume of liquid (units mg/g). The sorption capacity \( C_\infty \) is usually given in mass of dye per unit mass of porous material (units mg/g). Consequently, a natural choice for a non-dimensionalized concentration is given by

\[
\chi \equiv \frac{c\Theta_{tot}}{\Theta_{w, C_\infty}}
\]

where \( \rho_w \) is the solvent mass density.

**Length- and Timescales.**

The relevant geometric lateral length scale is the half-width of the line \( y_0 \), which we assumed to be on the order of 1 mm. Moreover, several timescales can be devised

1. an evaporation timescale given by the quantity of water present initially divided by the evaporative flux \( \tau_{\text{evap}} \equiv \frac{\theta_w(y = 0, t = 0)/(k_w(c_l(t = 0) - \rho_{\text{amb}}))}{\delta_y} \), with typical value \( \tau_{\text{evap}} \approx 10^3 \) s.
2. an adsorption timescale \( \tau_{ad} \equiv (k_w y_0)^{-1} \), with typical value \( \tau_{ad} \approx 10^3 \) s.
3. a desorption timescale \( \tau_{\text{de}} \equiv (k_{ad} y_0)^{-1} \), with typical value \( \tau_{\text{de}} \approx 10^3 \) s.
4. a convective timescale \( \tau_{\text{flow}} \equiv \frac{y_0}{v_{\text{Darcy}} (t = 0)} \), with typical value \( \tau_{\text{flow}} \approx 10^3 \) s.
5. a diffusive timescale \( \tau_{\text{diff}} \equiv \frac{y_0^2}{D_{\text{Darcy}}} \), with typical value \( \tau_{\text{diff}} \approx 10^3 \) s.

There is also a thermal timescale associated with evaporative cooling and heat exchange with the ambient environment; however, in this paper, we do not focus on thermal effects. For the relatively large length scales considered, the diffusive timescale is typically longer than the others, which implies that diffusive effects are negligible. Since \( \tau_{\text{diff}} \approx y_0^2 \), this may not hold for smaller line widths.

One can also define an evaporation-induced length scale as \( L_{\text{evap}} \equiv v_{\text{Darcy}}(t = 0)\tau_{\text{evap}} \) which is on the order of several centimeters and quantifies the maximum possible displacement of an imbibition front before complete evaporation.

**RESULTS AND DISCUSSION**

**Experimental Results—Drop Casting.** We performed drop-casting experiments using FSS and Rhodamine B solutions of different initial concentrations \( c_0 \) and the setup sketched in Figure 1a,b. Figure 1f shows the extracted retardation factor \( R_\ell \) as a function of \( c_0 \). The results qualitatively resemble those obtained by Koivunen et al. using the imbibition of tartrazine and safranine solutions from infinite reservoirs into porous layers that are comprised of calcium carbonate microparticles and polymeric binders.\(^{17}\)

**Experimental Results—Inkjet Deposition of Colorant Lines.** We performed inkjet deposition experiments using FSS and Rhodamine B solutions, and the setup is sketched in Figure 1c. We varied the substrate speed and the droplet ejection frequency, as quantified by the mass deposition rate \( m \). Figure 3a–e shows top view photographs of inkjet-deposited lines of an FSS solution (\( c_0 = 0.025 \) wt %) for a substrate speed of \( U_\ell = 0.2 \) mm/s and different mass deposition rates \( m \) of (a) 108, (b) 54, (c) 27, (d) 13.5, and (e) 6.75 \( \mu \)g/s on Mondi DNS HSI NF paper. The scale bar in (e) represents 1 cm. (f) Transverse widths of the wet zone \( \Delta y_w \) (open symbols) and the dye line \( \Delta y_c \) (filled symbols) as a function of \( m \). Diamonds correspond to FSS (\( c_0 = 0.025 \) wt %) and squares to Rhodamine B (\( c_0 = 0.015 \) wt %).
to two reasons: for lower moisture contents, the permeability of the porous medium is much smaller, such that the moisture front progresses relatively less far before evaporation is complete. Moreover, in the limit of low ink mass deposition, the quantity of the colorant per unit mass of paper eventually falls below the effective dye sorption capacity.

Figure 4a–e shows top view photographs of inkjet deposited lines of an FSS solution ($c_0 = 0.025 \text{ wt\%}$) for a mass deposition rate of $m = 27 \mu g/s$ and different substrate speeds $U_{IJ}$ of (a) 0.1, (b) 0.2, (c) 0.5, (d) 1, and (e) 2 mm/s on Mondi DNS HSI NF paper. The scale bar in (a) represents 1 cm. (f) Transverse widths of the wet zone $\Delta y_w$ (open symbols) and the dye line $\Delta y_d$ (filled symbols) as a function of $U_{IJ}$. Diamonds correspond to Rhodamine B ($c_0 = 0.015 \text{ wt\%}$) and squares to Rhodamine B ($c_0 = 0.025 \text{ wt\%}$) for experiments performed with constant values of $U_{IJ}$ and $m$.

The colorant is assumed non-volatile. Consequently, the moisture transport in a sheet of paper. In each plot, we focus on the effect of varying a single parameter (while keeping all others constant) on the chromatographic separation of the dye and the solvent. Unless specified otherwise, the values of the relevant parameters used in the simulations are those given in Table 1. Typical experimental values of the sorption capacity $C_m$ for cellulosic materials range between 0.5 and 100 mg/g. 

Typical experimental values of the dye adsorption timescale $\tau_{ad}$ for cellulosic materials range between 5 and 100 min. The larger values are typically ascribed to diffusive intra-material transport processes before adsorption can take place.

**Definition of Water and Colorant Front Positions.** For the definition of the water and the colorant front positions, we need to define appropriate concentration thresholds. Since evaporation is taken into account in the model, the quantity of water in the paper will decrease as a function of time. Due to the ICs and inherent symmetries, the moisture distribution will always assume its maximum at $y = 0$. Therefore, if we define a moisture content threshold relative to $\theta_{amb}(y = 0, t = 0)$, the corresponding front position will at all times be on the order of $y_0$ irrespective of the evaporative moisture loss. Therefore, we define a threshold relative to the *initial* dimensionless total moisture content as $0.035 \left[ \theta_{tot}(y = 0, t = 0) - \theta_{amb} \right]$. This implies that the moisture front position $y_{inf}$ defined as the maximum $y$-coordinate for which

$$\theta_{tot}(y, t) - \theta_{amb} > 0.035 \left[ \theta_{tot}(y = 0, t = 0) - \theta_{amb} \right]$$

holds, will start from $y_0$, first increase due to imbibition, reach a maximum, and eventually approach zero due to evaporation.

The colorant is assumed non-volatile. Consequently, the colorant concentration will tend to increase in time as the solvent evaporates. For this reason, we define the colorant threshold as 30% of the current maximum of the dye concentration $c_m$.

### Table 1. Parameter Values of the Base Case Considered in the Numerical Simulations

| Parameter | Value |
|-----------|-------|
| $k_{sl}$  | $1 \times 10^{-4} \text{m}^2/(\text{kg s})$ |
| $k_{ic}$  | $1 \times 10^{-4} \text{m}^2/(\text{kg s})$ |
| $C_m$     | 1 mg/g |
| $T_{amb}$ | 298.15 K |
| $k_{ed}$  | $2.8 \times 10^{-3} \text{m/s}$ |
| $y_0$     | 1 mm |
| $\theta_{amb}(y = 0, t = 0)$ | 0.98 $\theta_{amb}$ |
concentration. Analogously, the colorant front position $y_c$ is defined as the largest $y$-coordinate for which 
\[ C_c(t, y_{\text{tot}}) \leq 0.3 \max \{C_c(t, y_{\text{tot}})\} \] \hfill (19)

Here, the total mass of colorant per unit area of paper is defined as 
\[ C_{c,\text{tot}} = \rho \equiv \Theta_c + \Theta + \Theta_{c,\text{tot}} \] \hfill (20)

Figure 5a,b contrasts the dimensionless total moisture content profiles $\theta_{\text{tot}}(y) - \theta_{\text{amb}}$ for different times and (a) $k_\infty = 0$ (no evaporation) and (b) $k_\infty = 1.3 \times 10^{-2}$ m/s. The dashed horizontal lines indicate the threshold level defining the water front position. (c) Relative displacement of the moisture and colorant front positions $(y_w - y_0)/y_0$ (solid lines) and $(y_c - y_0)/y_0$ (dashed lines) as a function of time for different values of $k_\infty$ and $c_0$.

The blue and orange sets of curves correspond to simulations for $k_\infty = 0$, that is, the absence of evaporation. The water and colorant fronts increase monotonically in time. The yellow and purple curves correspond to simulations for $k_\infty = 1.3 \times 10^{-2}$ m/s. In this case, the water front reaches a maximum extension before retracting. At $t \approx 550$ s, the curves terminate because the moisture content everywhere falls below the threshold value of $0.035 \max \{C_c(t, y_{\text{tot}})\}$. The colorant front position saturates roughly when $y_c$ reaches its maximum.

As ICs, we used smoothed Heaviside functions for every variable, which drop from a constant value around $x = 0$ to the ambient value at a position $y = y_0$ [blue solid line in Figure 2a]. Thus, we can express the retardation factor as 
\[ R_f = \frac{\max(y) - y_0}{\max(y) - y_0} \] \hfill (21)

**Variation of Adsorption/Desorption Rates.** In Figure 6a,b, we present the retardation factor $R_f$ as a function of the initial concentration $c_0$ as extracted from 1D simulations for different values of (a) the adsorption rate $k_{ad}$, (b) the desorption rate $k_{de}$, and (c) the sorption capacity $C_\infty$. 

![Figure 6](https://doi.org/10.1021/acs.langmuir.1c01624)
extracted from 1D simulations. All curves exhibit a characteristic S-shape, that is, $R_t$ is independent of $c_0$ for both low and high values of $c_0$ and exhibits a transition zone from a lower to a higher value of $R_t$ that spans roughly 1 decade on the abscissa. The high-concentration value of $R_t$ is generally close to 1 because the dye concentration eventually exceeds the sorption capacity of the paper. The low-concentration value of $R_t$ strongly depends on the values of the adsorption rate $k_{ad}$ and the desorption rate $k_{ad}$. The transition zone is well described by the limits $1 \leq R_t \equiv \chi(t=0) \leq 10$.

An increase of $k_{ad}$ reduces the low-concentration value of $R_t$ because the dye is taken out of solution faster, which implies that it will be transported a shorter distance by the flow. An increase of $k_{ad}$ tends to increase the low-concentration value of $R_t$ because the adsorbed colorant enters back into the mobile liquid phase faster. Conversely, the limit of $k_{ad} \to 0$ (i.e., $\tau_{ad} \to \infty$) implies that the colorant is irreversibly adsorbed, which reduces its transport distance and thus $R_t$. The adsorption and desorption rates are therefore an antagonistic pair of parameters as far as their effect on $R_t$ is concerned.

We note that while $R_t$ approaches 0 for sufficiently large $k_{ad}$, $R_t$ may approach a non-zero value in the limit of small $k_{ad}$, as observed in Figure 6b. This is because desorption is only relevant after adsorption has taken place and a relatively small value of $k_{ad}$ (i.e., when $\tau_{ad} > \tau_{flow}$) can already enforce a finite value of $R_t > 0$.

**Variation of the Sorption Capacity $C_{∞}$**. The solid lines in Figure 6c illustrate the effect of varying the maximum sorption capacity $C_{∞}$ on the dependence of $R_t$ on $c_0$. Primarily, an increase of $C_{∞}$ shifts the transition zone toward proportionally higher values of $c_0$. The dashed lines correspond to simulations assuming a concentration-independent ink viscosity $\mu(c) = \mu(c = 0)$. For initial concentrations $c_0 > 1$ wt% and large retardation factors, a small deviation is observed.

**Variation of $y_0$ and the Initial Moisture Content**. In the line deposition experiments described in the section Experimental Results—Inkjet Deposition of Colorant Lines, the variation of $n$ and $U_0$ effectively changes the width and the moisture content of the deposited line, which serves as the IC for the 1D simulations of the dye redistribution. Therefore, we varied the parameters $y_0$ (line half-width) and the initial dimensionless moisture content $\theta_{init}(x = 0, t = 0)$ that characterize the IC [see Figure 2a]. Figure 7a-c illustrates the dependence of $R_t$ on $c_0$ for different values of $y_0$ and $\theta_{init}(x = 0, t = 0)$. In both cases, the highest sensitivity of $R_t$ with respect to parameter variations is observed in the transition region. A higher moisture content leads to an increase of $R_t$ over the entire range of initial concentrations. In contrast, a larger value of $y_0$ induces an increase of $R_t$ in the transition region and a decrease in the low-concentration regime.

The solid lines in Figure 7b represent the relative increase of the half-width of the colorant line $\max(y_c) - y_0$ as a function of $\theta_{init}(x = 0, t = 0)/\theta_{max}$ for different values of $c_0$. A higher moisture content always leads to a higher relative line broadening.

The solid lines in Figure 7d represent the increase of the half-width of the colorant line $\max(y_c) - y_0$ as a function of $y_0$ for different values of $c_0$. The dashed lines correspond to the maximum displacement of the moisture front $\max(y_m) - y_0$. In the limit of $y_0$ exceeding $L_{evap}$ all curves approach constant values, which implies that $R_t$ no longer depends on $y_0$ for large $y_0$. For small $y_0 < 0.5$ mm, $\max(y_m) - y_0$ scales approximately as $y_0^{1/2}$, whereas the colorant front displacement scales linearly.

\[ \max(y_c) - y_0 \sim y_0 \text{ for small } y_0 < 0.5 \text{ mm, which is the regime relevant to the printing of text documents and line drawings, } R_t \text{ thus increases with increasing } y_0. \]  The line width broadening is proportional to the line width, which implies that the relative line width broadening $\left[ \frac{\max(y_c) - y_0}{y_0} \right]$ is constant in this regime. This makes it particularly easy to compensate for the broadening effects in the development of print strategies for a given combination of dye, solvent, and substrate.

**Variation of the Evaporation Rate**. In inkjet printing, the evaporation rate can be enhanced, for example, by measures that increase the mass-transfer coefficient $k_{ev}$—such as adding external convection in the gas phase—or by increasing the ambient temperature, which increases the solvent vapor pressure and thus the difference between $\rho_{s}$ and $\rho_{amb}$. Evaporation has a strong effect on the time evolution of the water front position, as illustrated in Figure 5, and thus the time available for dye redistribution.

Figure 8a-c illustrates the effect of different mass-transfer coefficients $k_{ev}$ as well as different temperatures $T_{amb}$ on the dependence of $R_t$ on $c_0$. The retardation factor tends to increase with higher values of $k_{ev}$ and $T_{amb}$ except in the region where $R_t \geq 0.85$, where the curves essentially collapse. The biggest increment of $R_t$ occurs in the transition region.

The solid lines in Figure 8b,d represent the relative increase of the normalized colorant line width $\left[ \frac{\max(y_c) - y_0}{y_0} \right]$ as functions of $k_{ev}$ and $T_{amb}$ for different values of $c_0$. The dashed lines in Figure 8b represent the maximum relative displacement of the water front $\left[ \frac{\max(y_m) - y_0}{y_0} \right]$ which depends

![Figure 7](https://doi.org/10.1021/acs.langmuir.1c01624)  
**Figure 7.** (a,c) Retardation factor $R_t$ as a function of the initial concentration $c_0$ as extracted from 1D simulations for different values of (a) the dimensionless initial moisture content $\theta_{init}(x = 0, t = 0)$ and (c) the initial line half-width $y_0$. (b,d) Maximum displacement of the colorant (solid lines) and moisture (dashed lines) front positions as a function of (b) $\theta_{init}(x = 0, t = 0)/\theta_{max}$ and (d) $y_0$ for different values of $c_0$. 

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only weakly on \( c_0 \). The distance over which the water front spreads strongly depends on the effective evaporation rate. In contrast, the corresponding variation in \( [\max(y_c) - y_0]/y_0 \) is much weaker for initial concentrations \( c_0 \) below the transition region.

**Line Formation in Dye-Based Inkjet Printing on Paper.** In inkjet printing, individual droplets are deposited to generate arbitrary patterns. In the case of straight lines, it is usually desirable that the line width is as homogeneous as possible and does not exhibit undulations. If droplets are deposited with overlap, that is, with a center-to-center distance \( \Delta x_{\text{cc}} \) smaller than the footprint diameter \( 2R_{\text{drop}} \) [for definitions, see Figure 2b], then undulations tend to be reduced. However, the minimum achievable line width then increases. This is the regime relevant to our inkjet deposition experiments in the Section Experimental Results—InkJet Deposition of Colorant Lines.

**Figure 9a** illustrates the initial condition for an example of a 1D droplet array deposited with very small overlap, resulting in a large undulation amplitude at \( t = 0 \). **Figure 9b–d** compares the colorant and moisture distributions at \( t = 30 \) s for different values of \( c_0 \) corresponding to different values of the retardation factor \( R_f \). For a small \( R_f \leq 0.1 \) [case (b)], the initial undulation amplitude remains essentially unchanged, while the solvent has spread to more than 3 times the initial line width \( \langle w \rangle \) [for definitions, see Figure 2b]. For a medium \( R_f \sim 0.5 \) [case (c)], the undulation amplitude has decreased to about 50% of the initial value. For a large \( R_f \geq 0.9 \) [case (d)], the undulation is essentially gone completely, however, at the expense of a colorant line width \( \langle w \rangle \) increasing to about 3 times its initial value.

**Dye Precipitation.** At first glance, it is surprising that the retardation factors for Rhodamine B and FSS in Figure 1f differ so strongly, although the molecular weights are comparable and both dyes have a xanthene core. The values of \( c_{\text{cp}} \) at which \( R_f \) reaches a level of 0.5, differ by approximately a factor of 10. We believe the origin of the difference to be due to the presence of divalent \( \text{Ca}^{2+} \) ions due to the \( \text{CaCl}_2 \) loading in the paper. Hou and Baughman and Vimonses et al. have studied the precipitation of anionic dyes in water containing \( \text{Ca}^{2+} \). Analogous \( \text{Ca}^{2+} \)-induced precipitation effects had previously been observed for anionic surfactants.

**Figure 10a–d** presents the top view photographs after deposition of FSS solution droplets of different initial concentrations. The dashed circles approximately outline the maximum droplet footprint, as illustrated in Figure 1b. It is apparent that the color density and thus the dye concentration (per area of paper) have a local maximum at \( r = R_f \) for all values of \( c_0 \). We interpret this as a consequence of a concentration maximum of \( \text{Ca}^{2+} \) ions, which dissolve from the paper surface into the liquid droplet. Near the droplet contact line, the liquid thickness is the smallest. Thus, the ion concentration will be the highest (because the dilution of the \( \text{Ca}^{2+} \) ion concentration will be the smallest) and FSS precipitation will primarily occur there. A second reason is that after a brief initial phase, after ink imbibition in the thickness direction is complete, there is flow inside the droplet toward the contact line because non-zero moisture content gradients in the paper then exist only beyond \( r \geq R_f \). This phenomenon is akin to the evaporation-induced coffee-stain effect and transports the precipitated dye toward the contact line.

**Figure 10e–h** shows analogous images for Rhodamine-B solution droplets. The color density appears to be rather uniform for \( r < R_{\text{drop}} \) that is, behind the dye front and no contact-line, enhancement of the dye concentration is observed. This points at the absence of \( \text{CaCl}_2 \)-induced precipitation for the cationic dye.
while the cationic dye was apparently una
reaction of the anionic colorant on top of and inside the paper, order to facilitate colorant
mobility. A number of techniques have been developed in order to optimize the achievable resolution and pattern fidelity by improving and accelerating dye fixation. These include

(1) pretreatments by corona discharges and other plasmas,

(2) the incorporation of ionic compounds into paper that have the opposite charge polarity as the dye,

(3) the use of reactive dyes that form covalent bonds,

(4) the use of nanoporous coating layers that increase the effective surface area,

(5) the use of binders that reduce the permeability and thus the ink absorption rate, or

(6) an increase of the solvent evaporation rate by increasing the temperature or by using microwave or infrared irradiation to reduce the time available for ink transport.

In the framework of our adsorption model, strategies 1 to 4 aim at an increase of $c_\infty$ and $k_{ad}$ and/or a decrease of $k_{de}$, all of which tend to reduce $R_\infty$. Strategies 5 and 6 directly aim at minimizing solvent transport.

Our results are not only relevant to dye-based printing inks but also to pigment-based inks because the latter typically contain a number of molecularly dissolved additives that are subject to the same retardation phenomena as the dyes we investigated.

**CONCLUSIONS**

We have studied the transport and chromatographic separation of a model ink consisting of a dilute solution of a colorant in a solvent in thin porous media. We conducted systematic experiments using drop-casting and inkjet deposition of solutions of an anionic and a cationic dye in water on a commercial paper type. The paper was loaded with CaCl$_2$ in order to facilitate colorant fixation. This leads to a precipitation reaction of the anionic colorant on top of and inside the paper, while the cationic dye was apparently unaffected. The chromatographic retardation as a function of initial concentration of the two dyes differed by an order of magnitude despite their similar molecular weights and although both have a xanthene core.

We developed a comprehensive numerical model that accounts for unsaturated flow and chromatographic separation of a dye solution as well as the presence of permeable fibers, solvent evaporation, and heat-transfer effects. The model qualitatively reproduces the dependence of the retardation factor on the dye concentration. We have systematically varied the key parameters and evaluated their effect on the broadening and width fluctuations of inkjet-deposited colorant lines.

The sensitivity of the retardation factor $R_\infty$ to changes in operating conditions is generally the highest in the transition region, which spans roughly a decade in dye concentration in our model and where $R_\infty$ changes from a low-concentration to a high-concentration value. In order to optimize pattern fidelity, printing should be performed with the smallest moisture content, the highest adsorption and the lowest desorption rates, the highest evaporation rate, and the lowest dye concentration possible. In contrast, the reproduction of strong, saturated colors, however, requires a minimum colorant concentration depending on the paper type.

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**Author Contributions**

V.M. developed the experimental setup and the measurement protocols. He conducted all the experiments and analyzed the experimental data. The theoretical model was jointly
developed by G.V. and A.D. G.V. performed all the numerical simulations and analyzed the numerical data. The manuscript was written by V.M., G.V., and A.D. The research was conceived and guided by A.D.

**Notes**
The authors declare no competing financial interest.

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