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Transport and evaporation of aqueous co-solvent solutions in thin porous media

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A B S T R A C T

We have studied the imbibition and drying of water/co-solvent mixtures in paper and glass microfiber filters. The experiments reveal a rich interplay of solution imbibition, solvent evaporation and solvent-mediated pore-fiber transport. After deposition, liquids occupy the micron-scale inter-fiber pores of a paper sheet. In thermodynamic equilibrium, polar liquids such as water and co-solvents reside in the nm-scale intra-fiber pores of the cellulose fibers. The timescales for attaining equilibrium prove to depend sensitively on the water content, such that co-solvents can be temporarily trapped in a non-equilibrium configuration. The combination of two experimental methods allows the determination of both the overall co-solvent content and an estimation of what fractions reside in the pores and in the fibers of a paper sheet. The results are relevant to understanding the behavior of solutions in paper and provide insight into the dynamics of aqueous inkjet printing inks.

1. Introduction

Aqueous inkjet inks typically contain 5%-50% of co-solvents such as glycerol or glycols [1] for a variety of purposes: to serve as humectants [2], anti-cockle and anti-curl agents [2–5], viscosity modifiers [6], to increase the solubility of ink components with limited solubility in water [5,7], to aid gloss and to suppress coalescence as well as intercolor bleed [5]. Due to their low volatility, co-solvents typically remain in the paper for long periods after printing. The presence of a liquid can impart mobility to ink constituents, potentially impacting the long-term stability of a printed pattern. Therefore, understanding the distribution of the co-solvents during and after evaporation of the water is of relevance to the design and optimization of both inks and printing strategies.

Paper is a fibrous porous medium mainly consisting of cellulose fibers. Cellulose fibers typically have a hollow interior with a well-defined fiber wall with a thickness of a few micrometers [8]. The inter-fiber pore sizes are in the micrometer range, whereas the intra-fiber pores are of nanometer dimensions. For unsized paper, the fiber wall is highly permeable to water, which is a small molecule and reaches pore-fiber equilibrium within a timescale of typically a few seconds [9–11]. In contrast, for pure ethylene glycol (EG) it takes 20–400 times longer [9]. For larger molecules, the fiber walls can retard or prevent equilibration. Stone and Scallan devised a solute exclusion technique based on measuring the accessibility of intra-fiber pores to probe molecules of increasing molecular weight [12,13]. Typical cut-off values of the solute molecular weights are 250–5000 [14–16].
Hu and Brusseau studied the impact of the molecular weight of solutes on their transport through structured porous media that are characterized by a dual porosity with disparate pore lengthscales, similar to paper [17]. Yasuda et al. [18] investigated the transport of solutes through hydrated polymer membranes and found that the membrane permeability exponentially depends on the volume fraction of water. Paul et al. [19] studied solute transport through a particular type of membrane using a large variety of solvents and found that the key quantity determining solute permeability is the degree to which the solvent swells the membrane. Mackie and Meares [20] related membrane permeability to the tortuosity of the solute transport paths which depends strongly on the polymer volume fraction.

Due to their size difference, the permeability of the inter-fiber pores is much higher than that of the intra-fiber pores. Therefore, a retardation of the pore-fiber equilibration of co-solvents may induce an enhanced mobility of the ink constituents, possibly-causing them to be transported deeper into the paper. This can potentially affect the optical appearance and perceived print quality.

In this manuscript, two experimental methods are utilized to characterize co-solvent distributions in paper sheets and their time dependence: light transmission measurements [21–26] and capacitive tomography [27–29]. It is shown that while the latter is only sensitive to the total amount of co-solvent per unit area, the first is able to distinguish whether the co-solvent is residing in the micron-scale inter-fiber pores or inside the cellulose fibers. The combination of the two methods therefore allows for a comprehensive characterization of the co-solvent dynamics, especially the relevant timescales and the composition-concentration dependence of the pore-fiber transport.

Droplets of aqueous co-solvent solutions are deposited onto horizontal paper sheets using drop-casting. The droplet volume, the co-solvent concentration dependence of the pore-fiber transport.

### Materials and methods

Droplets of a specific volume \( V \) are placed on thin porous media and the subsequent imbibition and evaporation dynamics are characterized by light transmission imaging, impedance analysis and infrared thermography. All experiments are conducted under ambient conditions (temperature 24 ± 1 °C and relative humidity 30 ± 5%).

### 2. Materials and methods

#### 2.1. Materials

The following substrate materials are used:

- DNS High-Speed Inkjet NF paper (Mondi, grammage \( G = 80 \) g/m², thickness \( d_{\text{sub}} = 104 \) μm).
- Z-Plot 650 paper (Ziegler, \( G = 90 \) g/m², \( d_{\text{sub}} = 116 \) μm).
- Glass microfiber filter (Whatman, product number 1820-047 GF/A, \( G = 53 \) g/m², \( d_{\text{sub}} = 260 \) μm).

One key difference between the two paper types is that the NF paper is loaded with CaCl₂, while the Z-Plot 650 is salt-free. They are both unsized and uncoated. The papers are stored in a sealed container until each experiment to minimize humidity fluctuations.

Aqueous co-solvent solutions are made by mixing deionized water (Millipore Direct-Q3 R) and a pure co-solvent at a certain mass ratio in a glass bottle. Masses are measured with a Kern ALT 220-50AM scale. The co-solvents listed in Table 1 are purchased from Sigma-Aldrich and are used as-is to prepare solutions with initial weight fractions \( c_i \) of approximately 15, 20, 30, 40, 50 and 60 wt%. The exact weight fractions of the solutions are listed in Table 1 of the Supporting Information. For some experiments, the non-ionic surfactant Triton X-100 (Sigma-Aldrich, product number T9284, average MW 625, \( n_D = 1.491 \)) is added.

#### 2.2. Paper pre-treatments

In order to evaluate the impact of the paper composition on the degree of inhomogeneity of the co-solvent distribution, one of the following two methods of pre-treatment is employed for selected experiments:

1. To remove mobile paper constituents such as binders and salts, the paper sample is submerged in a 1 cm layer of deionized water for 20s while moving it. Subsequently, the paper is removed and left to dry for at least 2 h.
2. To increase the quantity of mobile paper constituents, the paper sample is placed in a UV-ozone cleaner (Jeligt, UV-cleaner model 42-220) for 2 or 10 min. Such treatment reduces the degree of polymerization of cellulose and other organic constituents, either by direct photolysis or photo-oxidative degradation, and creates reaction products of low molecular weight [38–40].

#### 2.3. Droplet deposition method and post-deposition treatment

Solution droplets are deposited onto the paper sample with a precision of 0.1 μl by means of a digital syringe (Hamilton, product number 800075, total volume 10 μl), fastened onto a labjack (Thorlabs, model 1490). During the light transmission experiments, the paper samples are suspended 6 mm above a glass surface. The approximate paper dimensions of \( 5 \times 6 \text{ cm}^2 \) are much larger than the diameter of the wet zone. The drying process progressed without any applied airflow under ambient conditions.

For some experiments to be discussed in Section 4.2, the following post-deposition treatment is performed: water is applied to the solution wet zone after it has dried for 30 min. First 0.2 ± 0.1 μl water droplets are deposited, with little to no overlap, using the digital syringe. After

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### Table 1

Material properties of pure co-solvents [31–37]. The values of viscosity \( \mu \) and surface tension \( \gamma \) are given for temperatures \( T \) of 20°C and 25°C, respectively. The refractive index \( n_p \) corresponds to a wavelength of 589 nm. The remaining columns provide the relative dielectric permittivity \( \varepsilon_r \) and the mass density \( \rho \) (\( T = 25^\circ \text{C} \)).

| Co-solvent          | prod. # | Purity  | MW       | \( \mu \) [mPa s] | \( \gamma \) [mN/m] | \( n_p \) | \( \varepsilon_r \) | \( \rho \) [kg/m³] |
|---------------------|---------|---------|----------|-------------------|-------------------|--------|-----------------|------------------|
| Glycerol            | 49770   | ≥ 99.5% | 92.09    | 1206              | 63.5              | 1.475  | 43              | 1258             |
| Ethylene glycol     | 324558  | ≥ 99.8% | 62.07    | 19.8              | 48.0              | 1.431  | 41.4            | 1110             |
| Diethylene glycol   | 32160   | ≥ 99.0% | 106.14   | 35.7              | 44.8              | 1.448  | 31.8            | 1113             |
| Triethylene glycol  | 90390   | ≥ 99.0% | 150.17   | 49.0              | 45.5              | 1.456  | 1120            |                  |
| Tetraethylene glycol| 110175  | ≥ 98.5% | 194.23   | 58.3              | 44.0              | 1.459  | 20.4            | 1121             |
| Polyethylene glycol | 90078   | –       | 300 ± 15 | 91.0              | –                 | 1.463  | 1122            |                  |

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2. Materials and methods

Droplets of aqueous co-solvent solutions are deposited onto horizontal paper sheets using drop-casting. The droplet volume, the co-solvent concentration and composition dependence of the pore-fiber transport.
5 min of drying, water is again applied, now generously with overlap, to fill up the wet zone, taking care not to extend it past its original boundaries.

2.4. Optical transmission measurements and image processing

Paper is a strongly scattering medium for visible light, because of the refractive index difference between cellulose \([41,42]\) \((n_{\text{cell}} \approx 1.48 \pm 0.015)\) and air \((n_{\text{air}} = 1.0)\) and since the typical lengthscale of the inter-fiber pore size distribution is close to the wavelength of light. Imbibition involves replacement of air by liquid, which significantly reduces the refractive index contrast and thus also the light scattering. This leads to an increase in light transmission from approximately 20\% for dry NF paper to about 50\% for NF paper saturated with water \([25]\).

A schematics of the experimental setup for light transmission is depicted in Fig. 1(a). A CMOS camera (Thorlabs Kira1x 1.3 MP, product number CS135MUN) is positioned 62 mm above an area light source (Advanced Illumination, model number 85257, center wavelength 660 nm). Pieces of paper are positioned 6 mm above the light source. Their azimuthal orientation with respect to the machine direction (MD) of the paper is kept constant. The camera exposure time and f-number of the lens are kept constant for all measurements. Images are recorded in 8-bit grayscale format.

First, the primary intensity \(I_0\) is acquired, measured without a sample and averaged over 60 frames to reduce noise. Similarly, the transmission of the dry paper is measured for 60 frames and averaged. Subsequently, the droplet is deposited and the light transmission intensity \(I\) in and around the wet zone is continually measured at a rate of 1 frame per second (fps). At regular time intervals \(\Delta t \geq 60\) s after the droplet has been placed, the subsequent 20 frames are averaged. The time averaged intensity distribution for dry paper \(I_{\text{dry paper}}(x,y)\) is subtracted from the time averaged intensity distribution \(I(x,y)\) of the wet paper for each time step. The resulting time-averaged intensity difference

\[
\Delta I(x,y) \equiv I(x,y) - I_{\text{dry paper}}(x,y) \tag{1}
\]

is divided by the primary intensity \(I_0\), resulting in the transmittance increment \(\Delta T/I_0\). This is occasionally multiplied by a brightness factor \(1 \leq b \leq 100\) to increase contrast and visibility. To compare intensity profiles at different time steps, cross-sections of the relative intensity distribution are extracted in the machine direction (\(y\)-axis) and the cross direction (\(x\)-axis) of the paper. These profiles are averaged transversely over 20 pixels.

2.5. Long-term light transmission measurements

Measurements with a duration of several days are conducted to investigate the slow pore-fiber equilibration dynamics of pure co-solvents. A droplet is placed on paper and left under ambient conditions for multiple days. The droplet size is 5\(\mu\)l for all glycols, while for glycerol the exact volume is unknown as the high viscosity precludes the use of a precision syringe. These light transmission measurements are recorded at 0.05 fps. Results are averaged over three consecutive frames. The transmittance \(I/I_0\) is evaluated as a function of time in the center of the deposited droplet, averaging over a 20×20 pixel\(^2\) area.

2.6. Calibration of transmittance vs. liquid content

The dimensionless liquid content \(\theta\) is defined as the ratio of the weight of liquid \(m_{\text{liq}}\) contained in a paper sample and its dry weight \(m_{\text{dry paper}}\)

\[
\theta \equiv \frac{m_{\text{liq}}}{m_{\text{dry paper}}} \tag{2}
\]

The correlation between transmittance \(I/I_0\) and \(\theta\) is calibrated for pure water, EG and TEG in NF paper, and for TEG in the glass micro-fiber filters.

A paper sample in equilibrium with the ambient atmosphere contains typically 0.05 – 0.1 g/g of moisture due to water absorption from the ambient humidity of the air \([43,44]\). As we are interested in liquid contents in the range 0 – 2 g/g, this ambient moisture contribution is neglected and an approximation of \(m_{\text{dry paper}}\) is determined by weighing it under ambient conditions.

For the calibration for pure water, the weight and transmittance of a paper sample are measured before it is submerged in water for 30 s. After withdrawal of the paper from the bath, both sides of the paper are wiped over a plastic surface once to remove excess water, after which the paper is placed between two transparent plastic plates to prevent evaporation. Subsequently, the weight \(m\) and the transmittance are measured. Next, the plastic plates are lifted to allow the paper to dry for 2 min. Subsequently, the sample is enclosed again and the next measurement data set is obtained. This process is repeated until \(m\) reaches \(m_{\text{dry paper}}\).

For EG and TEG, a different paper sample is used for each data point of the calibration graph. First, \(m_{\text{dry paper}}\) is measured. Next the sample is submerged in an aqueous co-solvent solution for at least 30 s. This is done at co-solvent concentrations between 0 and 100\%, with a different concentration for each sample. Next, the piece of paper is allowed to dry for at least 2 h. The essentially non-volatile co-solvents remain in the sample. The average and standard deviation of the transmittance \(I/I_0\) are evaluated over a 240×240 pixel\(^2\) area.

2.7. Capacitance measurements

The sample preparation method for the capacitance experiments slightly differs from the procedure outlined in Section 2.3. Circular, dry paper samples (diameter 12.7 mm) are placed on a thin-walled honeycomb grid, which provides mechanical support while at the same time facilitating water evaporation. Next, a 9.5\(\mu\)l solution droplet is deposited, allowing the wet zone to extend across the entire sample. Subsequently, the sample is left to dry for 90 min. For comparison with these as-deposited samples, also rehydrated samples were prepared, where multiple deionized water droplets of 0.2 ± 0.1\(\mu\)l are placed on the dried sample. After drying for 5 min, the same process is repeated three times, to ensure that the entire sample has been treated with water. The sample is then left to dry for 10 min before further use.

The paper samples are electrically insulated by placing them between two sheets of polyester foil (Folex, thickness 102 ± 1\(\mu\)m). This minimizes electrical conduction, which is very sensitive to the salt content of the paper. The electrical impedance is measured using an
impedance analyzer (Zurich Instruments, model MFIA) in the frequency range of 1 – 500 kHz. Cylindrical electrodes with a diameter \(d\), made of copper and coated with a thin layer of gold (\(d = 10\) mm) or stainless steel (\(d = 2\) mm), are mounted on plastic plates [see Fig. 1(b)]. Mechanical translation- and tip-tilt stages are used to align the electrodes. The electrode gap is \(450 \pm 5\) \(\mu\)m, leaving an air gap of approximately \(100\) \(\mu\)m between the electrodes after insertion of the sample. Effects of the heterogeneity of paper are essentially removed by spatial averaging due to the electrode diameter by far exceeding the thickness of the paper sheets.

2.8. Infrared measurements

The thermal processes accompanying droplet imbibition and water evaporation are investigated by infrared thermography. A paper sample is placed 68 mm below an infrared camera (FLIR, model A35sc, 320 x 256 pixels, spectral sensitivity range 7.5 – 13.5 \(\mu\)m). After droplet placement, the IR profiles are measured for up to 15 min at a frame rate of 1 fps. Systematic inhomogeneities in the IR images are corrected by recording an image of an isothermal object. Moreover, slight fluctuations in ambient temperature are monitored and removed from the IR images. To compare temperature profiles at different times steps, cross-sections of the temperature distribution are extracted in the cross-direction (x-axis) of the paper and averaged transversely over 20 pixels.

We estimate the absolute accuracy of the IR thermography data to be on the order of \(\pm 0.5\) K, whereas the relative accuracy, i.e. with respect to temperature differences within a recorded frame, to be on the order of \(\pm 0.2\) K.

3. Experimental results

3.1. Short-term time dependence

In Fig. 2(a–c), images of \(\Delta I\) for a TEG droplet (\(V = 5\) \(\mu\)l, \(c_0 = 40\) wt\%) are presented at different times after deposition. Bright regions indicate the presence of liquid in the pores. The wet zone has a slightly elongated, elliptical shape. Its major axis is aligned with the MD of the paper, due to the anisotropy of the cellulose fiber network. While \(\Delta I\) is relatively homogeneous at first, the formation of a ring structure is observed during later stages of the drying process. This effect is observed both with NF and Z-Plot paper.

In Fig. 2(d–g) cross-sectional profiles of \(\Delta I(y)/I_0\) along the MD through the center of the wet zone are plotted for different times after deposition. The intensity irregularities are due to the heterogeneity of paper and not due to noise. After 25 min, \(\Delta I/I_0\) has become stationary for the 40 wt\% TEG solution [Fig. 2(d)], as most of the water has evaporated. The ring formation is reflected in the presence of peaks at the edges of the wet zone, as indicated by the black arrows in Fig. 2(d). An analogous effect is observed for a 50% glycerol droplet in Fig. 2(e).

Fig. 2(fg) presents \(\Delta I(y)/I_0\) for pure water and pure TEG at different times after deposition. For pure water [Fig. 2(f)], the wet zone shrinks radially inwards upon drying, which is complete within 10 min. While a ring effect is not apparent at first, it is present for a short period of time and can be visualized with a high brightness factor \(b_y = 100\) (see Fig. 2 in the Supporting Information). Since this occurs in both the NF and salt-free paper, the phenomenon may be attributed to the presence of mobile additives in the paper other than salts, such as binders [45–47].

For pure TEG, which is essentially non-volatile, the wet zone expands and no ring effect is observed [Fig. 2(g)]. Moreover, the transmittance is larger than for pure water, due to the higher refractive index of TEG.

![Fig. 2](image-url)
3.4. Effect of droplet volume

This subsection elucidates the influence of the droplet volume \( V \) on the co-solvent distribution. In Fig. 5(a) light transmittance profiles \( \Delta I(y)/I_0 \) through the center of the wet zone are plotted for a 40 wt\% TEG solution and different values of \( V \). In all cases, distinct peaks of \( \Delta I(y)/I_0 \) are visible at the perimeter of the wet zone, which indicates that the ring formation is a robust phenomenon and not linked to a specific value of \( V \).

Fig. 5(b) shows the diameter of the wet zone \( d_{\text{wetzone}} \) as well as the width of the ring \( \delta_{\text{ring}} \) as a function of \( V \). The diameter of the wet zone \( d_{\text{wetzone}} \) is determined at an ordinate value of \( \Delta I/I_0 = 0.02 \), as illustrated in Fig. 5(a). The width of the ring with increased light transmission \( \delta_{\text{ring}} \) is defined as the full width at half maximum (FWHM) [Fig. 5(a)]. The red solid line in Fig. 5(b) is a linear fit, whereas the blue solid line represents the fit function \( d_{\text{wetzone}} = a + b(V - V_0)^{1/2} \), where \( a \), \( b \) and \( V_0 \) are fit parameters. This choice of fit function is inspired by mass conservation \( d_{\text{wetzone}}^2 \pi d_{\text{sub}} \sim V \), because for sufficiently large \( V \), the imbibition front penetrates through the entire thickness \( d_{\text{sub}} \) of the paper sheets. The ring width \( \delta_{\text{ring}} \) varies only weakly with \( V \). The numerical values of \( a \), \( b \) and \( V_0 \) are reported in the Supporting information, in addition to information about the reproducibility of the experiments, on which the error bars in Fig. 5 are based.

3.5. Capacitance measurements

Fig. 6(a) shows the capacitance increment \( \Delta C \equiv C_{\text{co-solvent}} - C_{\text{dry paper}} \) as a function of \( c_0 \) for three values of the measurement frequency \( f \) of the impedance analyzer. Solid symbols refer to untreated, as-deposited and open symbols to rehydrated samples. To within the experimental uncertainty, the capacitance values \( \Delta C \) are identical for treated and untreated samples. In the technologically relevant range shown (\( c_0 \leq 50 \text{wt\%} \)), \( \Delta C \) increases monotonically with \( c_0 \). Fig. 6(b)
shows a capacitance profile $\Delta C(x)$ measured with the $d = 2$ mm wide electrodes at $f = 50$ kHz across the center of the wet zone after deposition of a PEG-6 droplet ($c_0 = 40\%$, $V = 9.6 \mu l$) on NF paper. Fig. 6(c) presents a corresponding top-view photograph of the sample. The capacitance profile $\Delta C(x)$ has a maximum in the center of the wet zone, which might be related to a higher residual water content, due to the higher relative dielectric permittivity of water ($\epsilon_r = 80.1$) compared to TEG ($\epsilon_r = 20.4$). There seems to be no clear correlation between $\Delta C(x)$ and the ring formation visible in the light transmission images.

### 3.6 Infrared measurements

Fig. 7(a,b) depicts temperature maps $T(x,y)$ obtained with IR thermography 60 s after deposition of a TEG solution droplet ($c_0 = 40\%$ wt) and a pure TEG droplet, respectively. For pure TEG, the temperature increases in the wet zone, as water condenses due to the hygroscopic nature of glycols. On the other hand, water evaporates from the 40 wt% TEG solution, causing a temperature drop due to evaporative cooling. Despite the difference in $V$, the wet zone at $t = 60$ s is smaller for pure TEG than for the 40 wt% TEG solution, most likely due to the higher viscosity of pure TEG. Cross-sectional profiles $T(x)$ through the center of the wet zone are presented for different times and different liquid compositions in Fig. 7(c–f). A higher temperature difference is observed for aqueous solutions subject to evaporative cooling than for pure co-solvents subject to condensation heating.

The temperature profiles return to an isothermal state $T = T_{amb}$ within approximately 15 min. The pure water droplet takes slightly longer to dry than the 40 wt% TEG droplet, because more water needs to evaporate due to differences in composition and volume. The glycerol droplet also takes slightly more time to equilibrate thermally. Due to its high viscosity, it does not spread and imbibe into the paper as quickly. Rather, at $t = 15$ min, a significant portion of the glycerol still resides on top of the paper in the form of a droplet with relatively small surface area.

It is instructive to compare the timescales within which the light transmission in Fig. 2(d) and the temperature in Fig. 7(c) reach their steady-state values for a 40 wt% TEG solution. These are approximately 7 min and 12 min, respectively. We attribute the difference to the drying dynamics of paper. We hypothesize that upon drying, water is first depleted from the inter-fiber pores, as the capillary pressure there is less negative than in the fibers. Moreover, the fiber walls act as an obstacle to water vapor transport to the ambient gas phase. As the water contained in the fibers does not affect the light-scattering power of paper significantly, this would explain why the light transmission reaches a steady-state first. Water continues to evaporate from the fibers – although at a lower rate – as reflected by the diminishing temperature amplitude $|T - T_{amb}|$. We note that the thermal equilibration time of dry NF paper with the ambient atmosphere is on order of 10 s [49], i.e. the much slower temperature evolution in Fig. 7 primarily reflects the time dependence of the water evaporation rate.

---

**Fig. 5.** (a) Relative light transmission profiles $\Delta I(y)/I_{ref}$ through the center of the wet zone for TEG ($c_0 = 40\%$) droplet volumes $V = 1, 2, 5$ and $10 \mu l$ in NF paper after 25 min of drying. (b) Corresponding average diameter $d_{wet\ zone}$ of the wet zone (left ordinate axis) and width of the ring $\delta_{ring}$ (right ordinate axis), as a function of the droplet volume $V$.

**Fig. 6.** (a) Capacitance increment $\Delta C$ as a function of $c_0$ for three values of the measurement frequency $f = 5, 50$ and $500$ kHz of the impedance analyzer. The $d = 10$ mm wide electrodes are used. Solid symbols refer to as-deposited solution droplets and open symbols to samples that were rehydrated 90 min after deposition. Triangles refer to Z-Plot paper, all other symbols to NF paper. (b) Capacitance profile $\Delta C(x)$ measured with $d = 2$ mm and $f = 50$ kHz through the center of the wet zone after deposition of a PEG-6 droplet ($c_0 = 40\%$, $V = 9.6 \mu l$) on NF paper. (c) Corresponding reflection image. The error bars in (a,b) are representative for all data points.
3.7. Long-term light transmission experiments

In order to characterize the timescales of the pore-fiber transport process, long-term transmission measurements are conducted after deposition of droplets of pure co-solvents. The resulting average values in the center region of the wet zones are depicted in Fig. 8(a).

All co-solvents show an initially rapid decrease of $I/I_0$ in time followed by a slower decrease. Three phenomena contribute to the decrease of the transmittance. First, due to lateral expansion of the wet zone, the liquid content per area decreases, see e.g. Fig. 2(g). Secondly, the co-solvents migrate from the pores into the cellulose fibers, where they become essentially invisible as far as light scattering is concerned. Lastly, evaporation may occur. However, the vapor pressure of co-solvents is very low and evaporation is assumed to be negligible, with the possible exception of EG.

The co-solvents differ significantly regarding the timescale with which the transmittance of dry paper $I_{\text{dry paper}}/I_0$ (dashed line in Fig. 8(a)) is approached. The transmittance of EG decays to a stable value close to $I_{\text{dry paper}}/I_0$ within 8 h. The decay is slower as the MW of the glycols increases. The transmittance of glycerol remains far above $I_{\text{dry paper}}/I_0$. Moreover, fluctuations in the transmission are observed due to fluctuations in ambient humidity. Fig. 8(b) shows the area of the wet zone $A_{\text{wet zone}}$ as a function of time for TEG. The area is obtained by counting pixels that exceed a transmittance of $I/I_0 > 0.25$. Fig. 8(c) shows the maximum area $A_{\text{max}}$ of the wet zone of the glycols as a function of co-solvent MW and viscosity. For glycol co-solvents, $A_{\text{max}}$ exhibits an approximately linear correlation with both MW and $\mu$.

In a porous medium with impermeable fibers, the viscosity would only affect the time required for $A(t)$ to reach $A_{\text{max}}$, but not the value of $A_{\text{max}}$. In paper, the pore-fiber transport rates decrease with increasing MW [13–16]. This agrees with the findings in Fig. 3(h). Thus, co-solvents reside in the inter-fiber pores longer for higher MW. The permeability of the pores is much higher than that of the fibers due to the larger dimensions. Therefore, even though imbibition takes longer for larger values of $\mu$, the maximum area nevertheless increases with MW, because the pore-fiber transport depends more sensitively on MW.

3.8. Effect of paper pre-treatment and surfactants on ring formation

Since a ring with increased light transmission is also observed for pure water (see Fig. 2 in the Supporting Information), the presence of additives in the paper may play a role. Two methods of pretreatment are employed, as discussed in Section 2.3, to respectively increase and decrease the amount of mobile constituents in the paper. Fig. 9(a–d) compares light transmission images of untreated NF paper with pore-fiber transport eventually reducing the transmittance below the threshold value of $I/I_0 > 0.25$. Fig. 8(b) shows the area of the wet zone $A_{\text{wet zone}}$ as a function of time for TEG. The area is obtained by counting pixels that exceed a transmittance of $I/I_0 > 0.25$, which is slightly above $I_{\text{dry paper}}/I_0$. $A_{\text{wet zone}}$ first increases due to lateral spreading, as illustrated by Fig. 2(g), reaches a maximum value $A_{\text{max}}$ and then decreases, because both the lateral spreading and continued...
those of washed NF paper and NF paper after 2 and 10 min of ozone treatment. The ring is less visible for the washed NF paper, while it is much more pronounced for the UV-ozone treated paper. This implies that the amount of mobile constituents in the paper has an effect on the involved transport processes, and possibly the pore-fiber equilibration. However, since washing and drying of paper induces irreversible structural changes, little can be said about the precise origin of the differences compared to untreated paper.

Surfactants are common additives in water-based inkjet printing inks. A more pronounced ring is visible in Fig. 9(e) for a solution of 38 wt% TEG and 5 wt% Triton X-100 compared to 40 wt% TEG in untreated NF paper in Fig. 9(a). This could be a consequence of the high MW of 625 of Triton X-100, because of which it is likely excluded from the fiber interiors. Moreover, the refractive index of Triton X-100 is an even better match to that of cellulose compared to TEG.

In glass microfiber filters, the fibers are hydrophilic but impermeable and no binders are present. Fig. 9(f) shows that no ring is visible after deposition of a 5 μL 40 wt% TEG droplet. The diameter of the wet zone is smaller due to the higher substrate thickness of 260 μm. This suggests again that the emergence of a ring structure is linked to the presence of permeable fibers and mobile constituents of high MW.

4. Discussion

4.1. The failure of co-solvent quantitation based on light transmission alone

In a previous study [25], light transmission imaging is used to unambiguously determine the local moisture content \( \theta_{\text{loc}}(x, y, t) \) by performing a calibration of \( I/I_0 \) as a function of \( \theta_{\text{loc}} \) using samples of known \( \theta_{\text{loc}} \). In this research, the attempt is made to apply the same metrology principle to the case of aqueous co-solvent solutions. The solid symbols in Fig. 10 represent the resulting calibration curves for EG and TEG in NF paper in pore-fiber equilibrium. For comparison also a calibration curve for pure water (black squares) is shown. Typical standard deviations are depicted by error bars. Those of all calibration samples are provided in the Supporting Information.

The transmittance curves \( I/I_0 \) for NF paper monotonically increase with increasing \( \theta \) until they reach plateaus at \( \theta_{\text{loc}} \approx 1.25 \) and \( \theta_{\text{T,TEG}} \approx 1.4 \). These threshold values of the liquid content are related to the maximum holding capacity of paper. If we assume that water and glycols equally swell the paper, then the saturation point for water should occur at a lower liquid content, because its mass density is about 11% lower than that of EG and TEG (see Table 1). The plateau values of \( I/I_0 \) are identical for TEG and EG to within experimental uncertainty, but significantly lower for water, because the refractive index of the glycols is much closer to \( n_{\text{cell}} \).

The open symbols in Fig. 10 represent droplet deposition experiments using 60 wt% solutions of EG and TEG as well as pure TEG on NF paper, and 40 wt% TEG on the glass micro-fiber filters. The liquid content is determined from \( A_{\text{wet zone}} \) and \( V \), taking into account the hygroscopic nature of the co-solvents. The datapoints of the pure TEG droplet correspond to the first hour after deposition. The transmittance \( I/I_0 \) decreases as time progresses, which is related to the expansion of the wet zone as visible in Fig. 2(g).

The transmittances for the droplet experiments on NF paper are higher than the calibration curves. The current hypothesis is that this difference is due to the inability of co-solvent solutions with high c₀ and high MW to reach a configuration corresponding to pore-fiber equilibrium in the time available until the water has evaporated. Rather, the co-solvents are predominantly left in the micron-sized inter-fiber pores, where their presence strongly reduces the light scattering. In contrast, in equilibrium the co-solvents would predominantly reside inside the cellulose fibers for \( \theta \ll 1.4 \). There, the relevant structural length-scales are much smaller than the wavelength of the light source, such that the co-solvents do not significantly contribute to the overall light scattering strength.

The calibration curve for the glass micro-fiber filters is less steep and reflects a higher holding capacity than for NF paper, due to the larger substrate thickness and higher porosity. As expected, the droplet measurement (open diamond) coincides with the calibration data (solid diamonds) for this substrate, which consists of impermeable fibers. Commercial printing papers commonly contain a number of components such as fillers and binders. Paper manufacturers generally do not disclose their chemical composition, nor the quantities added. We expect that inorganic pigment filler particles affect the transmittance of paper, as their refractive indices are likely not matched to \( n_{\text{cell}} \). For instance, calcite has \( n \approx 1.49 – 1.65 \), for talcum \( n \approx 1.54 – 1.60 \), for kaolinite and illite, which are common constituents of clay, \( n \approx 1.55 – 1.57 \) and 1.53 – 1.60, respectively [50]. In view of co-solvents being almost index-matched to cellulose, it is likely the presence of filler particles that causes the transmittance of co-solvent saturated NF paper to be about 65% in Fig. 10 and not higher. This hypothesis is
supported by the transmittance results for the glass micro-fiber filter (α ≈ 1.51), which does not contain any fillers and which reaches a maximum value of $I/I_0$ of at least 82%.

### 4.2. Pore-fiber transport

We conclude that the timescale of pore-fiber equilibration of co-solvent solutions depends sensitively on the concentration. A higher amount of water allows the co-solvent to migrate into the fibers faster, as the water plasticizes and swells the fiber walls. Fig. 2(f) shows that the water evaporates from the outside inwards. Consequently, the concentration of water at the perimeter of the wet zone is lower than in its center. No significant chromatographic retention of the co-solvent is observed except possibly in Fig. 4(b), probably due to the high co-solvent concentrations and the short migration distances. Thus, the co-solvent concentration at the edges is expected to be higher than in the center of the wet zone during the drying process. Consequently, less of the co-solvent is transported into the fibers and more remains in the pores at the perimeter, than in the center of the wet zone. Since the co-solvents affect light transmission primarily when they reside in the inter-fiber pores, but not when they reside in the fibers, this would explain the formation of the bright ring observed in Figs. 2, 3 and 4.

This hypothesis is further tested by studying changes in transmittance in the wet zone of a 50 wt% TEG droplet upon rehydration by means of local deposition of water, as discussed in Section 2.3. The transmittance $I/I_0$ after deposition of a 50 wt% TEG droplet and after a drying time of 25 min is presented in Fig. 11(b). Fig. 11(c) depicts $I/I_0$ after local application and drying of a 50 wt% TEG droplet. The black spots in the wet zone coincide with the locations where water has been applied. After rewetting the entire wet zone, the bright region has almost completely disappeared as illustrated in Fig. 11(d). Since the TEG does not disappear from the paper, we attribute this decrease in transmittance to the solvent-assisted migration of TEG from the inter-fiber pores into the fibers after water application, rendering it ‘invisible’ to a transmission measurement and confirming the aforementioned hypothesis.

### 5. Summary and conclusions

In this study, the imbibition and drying behavior of aqueous co-solvent solutions in paper sheets is characterized using light transmission and impedance spectroscopy experiments. The transmittance of a paper sheet is primarily determined by light scattering, which depends strongly on the lengthscale of the refractive index heterogeneities, i.e. the size of the pore fractions unoccupied by liquid. The inter-fiber pores of dry paper are in the micron size range, which highly scatter visible light and account for its relative intransparency. The intra-fiber pores are in a size range of 1–20 nm, which do not significantly contribute to the light scattering power. Thus, the migration of co-solvents from the pores into the fibers is accompanied by a strong increase in opacity. In contrast, impedance spectroscopy is sensitive only to the total quantity of co-solvent present in a paper sample. Consequently, the combination of these two experimental methods is not only able to quantify the amount of co-solvent present in a paper sheet, but also to determine whether it is located in the pores or in the fibers.

The pore-fiber migration rate is highly sensitive to the local co-solvent concentration, as water is required to first swell and plasticize the fiber walls, before co-solvents of high MW can pass into the fiber interior. Since the water concentration after droplet deposition tends to be lower at the perimeter of the wet zone, inhomogeneous pore-fiber distributions result. This induces the formation of a ring with increased transmittance at the perimeter of the wet zone. Its appearance is reminiscent of the well-known coffee stain effect, but it has a fundamentally different origin.

CRediT authorship contribution statement

**M.G. Wijburg:** Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **S. Wang:** Investigation, Formal analysis, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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