Ink-Jet Printing with Inks that Phase Separate During Drying

Ashley S. Johns and Colin D. Bain; Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, United Kingdom

Abstract

Ink-jet formulations that have been designed to phase separate upon deposition onto the substrate have been investigated using model fluids. A physical model of expected separation behavior for an aqueous solution of butanol suggested that the butanol-rich phase would form at the contact line as an annular ring. The surface tensions in air of the saturated fluids and the interfacial tension between them were combined with measured contact angles on the substrate to show that the butanol-rich phase would partially undercut the water-rich phase. Printing trials with a 6 %wt butanol solution, however, did not show phase separation and the observed internal Marangoni flows were consistent with the more rapid evaporation of butanol than water. The origin of this behavior is the highly non-ideal vapor pressure for butanol at saturation. A criterion for predicting whether or not a particular mixture would phase separate was developed based on the non-ideal component vapor pressures. Aqueous glycol ether solutions show the correct properties and a 15.1 %wt dipropylene glycol methyl ether acetate solution displayed phase separation. Separation occurred first at the contact line and the phase boundary moved radially inwards until water evaporation was complete.

Introduction

Ink-jet formulations are highly tailored so that desired properties are manifested at every stage of a process. Effective design requires a detailed knowledge of fluid dynamics and of the chemical, physical and rheological properties of the materials implemented. The nature of formulations therefore differ widely depending on their requirements. For graphics applications, pigments are often delivered as aqueous dispersions with additives incorporated to stabilize the particles, modify the viscosity, control spreading behavior on the substrate, reduce the occurrence of bubbles and prevent jetting failure after an idle period [1]. Once a drop arrives on the substrate, control over drying dynamics and deposit morphology can be exerted. Collection of solids at the drop periphery under convective flow [2] can be prevented using additives to generate surface tension gradients that give rise to internal flows [3]. Strategies for controlling particulate migration using formulation rheology have been demonstrated [4].

When designing functional inks, the overall miscibility of all the components is an important consideration and solvent mixtures are often used to optimize the solubility of active ingredients. Such mixtures are chosen to be fully miscible. Many pairs of liquids are, however, only partially-miscible and exist as one phase over a limited range of compositions. If the minor component were to be present at a concentration above its solubility limit, a second phase rich in that species would form. We posed the question of how an ink-jet formulation would behave if a partially-miscible solvent pair were

deliberately chosen so that phase separation occurred during evaporation of a droplet on a substrate.

For a mixture to phase separate when printed, the components must be partially miscible. The formulation would be in a single phase during printing, with the minor component present at a concentration close to its solubility limit. For a spherical cap with a contact angle less than 90°, the evaporative flux is greatest at the contact line [2]. We would therefore expect the second phase to form first at the drop contact line since it is there that the composition changes the fastest. If the major component is the more volatile, the drying drop would be enriched in the minor component until the local composition passed through the binodal and phase separation occurred. (Supersaturation is also possible if nucleation of the new phase is slow; in this case, phase separation may not occur until the spinodal composition is reached.)

Our aim is to discover if phase separation influences the way a drop dries and whether it could provide an interesting control mechanism for deposit morphology. One can imagine that dynamics of phase separation could proceed in a number of directions. Were the newly formed minor phase to remain as an annular ring, there is the possibility of disrupting the outward convective flow commonly observed for pinned drops. At equilibrium, the vapor pressure of a component must be the same in each of the liquid phases in contact. During evaporation, the major component must diffuse into the phase rich in the minor component to maintain a constant vapor pressure for that component over the drop surface. Were diffusion across the liquid-liquid interface to become evaporation-limiting, as opposed to diffusion in the vapor [2], a change in behavior from outward convective flow might be expected. There is also opportunity for patterning if a second phase were to form as an annular ring: were there a pair of solutes present that each favored dissolution in opposing phases, they could be deposited as concentric circles. Alternatively, the new phase could completely undercut the major phase so that the former maximized its contact with the substrate. A particulate or solvated material present in the major phase could then be allowed to aggregate before adhesion to the surface.

Here we present results for model phase-separating candidates that were ink-jet printed onto hydrophobized glass substrates, where the drying process was captured from below and from the side using high-speed cameras. We start by considering water and butanol mixtures because the components are partially miscible, with butanol dissolving in water up to 7.6 %wt. The minor component also has a smaller vapor pressure than the major component, having 0.93 and 3.14 kPa at 298 K, respectively [5]. A theoretical picture of how we might expect the system to appear when it phase separates is constructed based on physical data. The results of printing aqueous solutions of butanol are contrasted against those of aqueous solutions of dipropylene glycol methyl ether acetate (DPGMEA). Observations are discussed with the wider aim of identifying a criterion for selecting systems that would phase

separate upon printing, providing opportunities for advanced patterning techniques.

Experimental

Two candidates for phase-separating formulations were trialed: aqueous solutions of DPGMEA and aqueous solutions of butanol. DPGMEA (*Sigma-Aldrich*, 99%), Butan-1-ol (*Fisher*, AR) and water (MilliQ) were used as received. DPGMEA has been reported, at 298 K, to reach saturation in water at 16.0 %wt, whilst water reaches saturation in DPGMEA at 3.5 %wt [6]. The mutual solubilities of butanol and water were determined experimentally by dropwise addition of one material to the other. The mixture was said to be saturated when mixture cloudiness completely obscured text over a path length of 3 cm under visual inspection. At 294 K, Butanol reached saturation in water at 7.6 %wt and water reached saturation in butanol at 20.1 %wt.

Interfacial tensions were measured using a pendent drop tensiometer (*First Ten Ångstroms*, FTÅ200) mounted on an anti-vibration table. All materials that came into contact with the fluids had been thoroughly bath sonicated in dilute alkaline detergent solution (*Decon Laboratories*, Decon90), rinsed with water (MilliQ) and dried in an oven. Fluids were placed into cuvettes and air bubbles formed using a syringe and a J-shaped needle. The arrangement was positioned in front of a light source such that a camera (*Watec*, Wat-902B) attached to the back of a telescopic lens viewed the bubble as a silhouette. Images were captured using proprietary software (*First Ten Ångstroms*, Fta32 v2.0) and calibrated with a sphere of diameter 3 mm. Fluid densities were determined using a pycnometer and surface and interfacial tensions were found by solving the Laplace-Young equation analytically. The surface tension between air and a 7.6 %wt butanol solution in water, $\gamma^{\mathrm{WA}}_{\mathrm{sat}}$, is 24.1 ± 0.7 mN/m. The surface tension in air of a 20.1 %wt water solution in butanol, $\gamma^{\mathrm{OA}}_{\mathrm{sat}}$, is 23.3 ± 0.2 mN/m. A drop of 7.6 %wt butanol solution was suspended in a 20.1 %wt water solution in order to determine the interfacial tension present between the saturates, $\gamma^{\mathrm{WO}}_{\mathrm{sat}}$, which was observed to be 1.6 ± 0.1 mN/m.

Contact angles of the saturated solutions for the butanol-water system were measured on a glass substrate with a hydrophobic coating. The substrates were typically prepared by bath sonicating glass coverslips in acetone for 15 minutes and then in 1−2 %wt alkaline detergent solution (*Decon Laboratories*, Decon90) for 1−2 hr. They were then rinsed in water (Milli-Q) and dried at 110° for 1 hour. Hexamethyldisilazane (*Alfa Aesar*, >98%) was deposited on the surfaces by vapor deposition in a vacuum desiccator overnight. The coated substrates were rinsed in water and dried under an argon flow. Measurements of the contact angle were made using the tensiometer imaging system. To measure the contact angle of the saturated solutions in air, the substrate was placed within a glass cell that was saturated with vapor. A spherical fit for water-saturated butanol yielded $\theta^{\mathrm{WA}}_{\mathrm{sat}} = 10 \pm 4°$ at 295 K. The contact angle of the water-rich solution in the butanol-rich solution was measured by dispensing a drop of the former onto the substrate when it had been submerged in the latter. Fitting a non-spherical profile to the drop yielded a contact angle, $\theta^{\mathrm{WB}}_{\mathrm{sat}}$, of 117 ± 4° at 295 K.

Printing experiments were carried out on a bespoke inverted microscope (Fig. 1). A formulation was placed in a reservoir and an overpressure used to move fluid through a capillary to the printhead (*MicroFab*, MJ-ABP-01). The
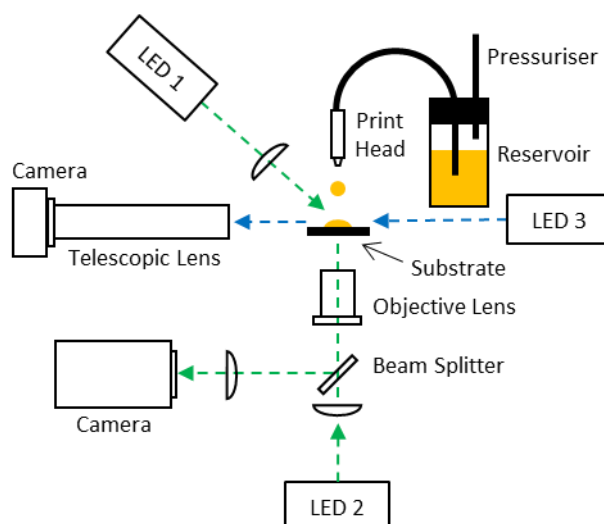

Figure 1. *Schematic diagram of the rig used to print emulsion drops and image the drying process. Three LEDs were implemented to allow recording to take place on two high-speed cameras simultaneously from the side and from below. Unlabeled optics are plano-convex spherical lenses.*

printhead has an orifice of diameter 50 μm and is actuated by a symmetrical bipolar wavefunction generated by a driver (*MicroFab*, JetDrive III Controller). Drops were deposited onto the hydrophobized substrate positioned directly below. The drops were illuminated from above by an obliquely mounted LED (*Thorlabs*, 505 nm, LED 1) and from below (*Thorlabs*, 505 nm, LED 2). The former source scatters at interfaces within the drop, allowing the movements of particulates to be tracked, whilst the latter is a simple brightfield source used in reflection. Light from both LEDs was collected by an objective lens (*Olympus*, 50×, NA 0.5) mounted below the substrate and passed to a high-speed camera (*Photron*, FASTCAM APX RS), via a beam splitter and a plano-convex spherical lens. The drop was also illuminated in profile by another LED (Beaglehole Instruments, 455 nm, LED 3) mounted to the side and images were collected using another high-speed camera (*Optronis*, CR450x3), equipped with a telescopic lens (*LaVision*, 12× Zoom Lens). Images of the drop from below and from the side were both calibrated against arrays of dots of known diameter and spacing (*LaVision*, Micro Calibration Plate). Information about the drop volume and contact angle over time was found using a custom MATLAB routine that fitted spherical caps to images collected of the drop from the side.

Results and Discussion

The first system to be investigated for phase separation upon jetting was butanol-water. For phase separation to be observed for the mixture, the minor component needs to increase in concentration until it passes through the binodal and therefore needs to evaporate more slowly than the major component. The rate of evaporation [7] for a spherical cap of material A, r_{A}, is proportional to its partial vapor pressure p_{A} and its diffusion coefficient in air, D_{A}:

$$r_{\mathrm{A}} \propto p_{\mathrm{A}} D_{\mathrm{A}}. \tag{1}$$

For water, the relative humidity, *RH*, must also be taken into account:

$$r_{\rm w} \propto p_{\rm w} D_{\rm w} \left(1 - RH\right). \tag{2}$$

For evaporation into stagnant air, the proportionality coefficient depends on the drop radius and contact angle. For the situation where a volatile solute, B, increases in concentration until it supersaturates, $r_{\rm B}x_{\rm A} < r_{\rm A}x_{\rm B}$. Conversely, if $r_{\rm B}x_{\rm A} > r_{\rm A}x_{\rm B}$, the concentration of B decreases with time and the drop remains as a single phase throughout drying. Therefore defining κ as

$$\kappa = \frac{r_{\rm A}x_{\rm B}}{r_{\rm B}x_{\rm A}}, \tag{3}$$

the quantitative criterion for the observation of phase separation is $\kappa > 1$.

In an ideal binary solution, the vapor pressure of a component, $p_{\rm A}$, is calculated from the vapor pressure of the pure liquid, $p_{\rm A}^*$, according to Raoult's law,

$$p_{\rm A} = x_{\rm A}p_{\rm A}^*. \tag{4}$$

The vapor pressures of pure water and n-butanol are 3.14 kPa and 0.93 kPa at 298 K, respectively [5]. Butanol has a mole fraction of 0.02 at saturation [8]. At 298 K, the diffusion coefficients for water and butanol are 0.25 and 0.09 cm²/s, respectively [9]. Assuming ideal vapor pressures and that $RH = 0.4$, $\kappa^{\rm raoult} = 5.6 \gg 1$, suggesting that water–butanol mixtures would be a good candidate for a phase separating mixture.

For a spherical cap with a contact angle of less than 90°, evaporative flux is greatest at the contact line [2]. Were an aqueous solution of butanol to phase separate upon deposition from an ink-jet printhead, we would then expect the butanol-rich phase to form at the contact line because that is where composition is changing the fastest. A physical model of how the butanol-rich and water-rich phases would behave were they brought into contact can be deduced using physical data. The spreading coefficient, $S^{\rm O}$, for the butanol-rich phase resting on the water-rich phase in air is defined in terms of the surface and interfacial tensions according to

$$S^{\rm O} = \gamma^{\rm WA} - \left(\gamma^{\rm WO} + \gamma^{\rm OA}\right). \tag{5}$$

Using $\gamma^{\rm WA}_{\rm sat} = 24.1$ mN/m, $\gamma^{\rm OA}_{\rm sat} = 23.3$ mN/m and $\gamma^{\rm WO}_{\rm sat} = 1.6$ mN/m, $S^{\rm O} = -0.8$ mN/m. A negative value of $S^{\rm O}$ indicates that the oil will not wet the aqueous surface thermodynamically. The butanol-rich phase will therefore form a lens when resting on the water-rich phase in air. The lens will possess specific contact angles above and below the air-water surface in order that no net force is present at the three-phase contact line. The contact angles are readily calculated from Neumann's triangle. Taking an annular ring of the butanol-rich phase at the contact line of an ink-jet printed drop, the behavior of the water and butanol saturates can be predicted by resolving forces at the three 3-phase contacts: (1) The butanol-rich liquid on the substrate in air has a contact angle of 10°; (2) the water rich phase on the substrate and submerged in the butanol rich phase has a measured contact angle of 117°; (3) the two saturates in air have equilibrium angles derived from the measured surface and interfacial tensions and are displayed in Figure 2. The sum of internal angles for the butanol-rich phase is 135°, significantly less than the 180° required for the interfaces to be straight. The interfaces must, therefore, be curved. The Laplace pressure is given by
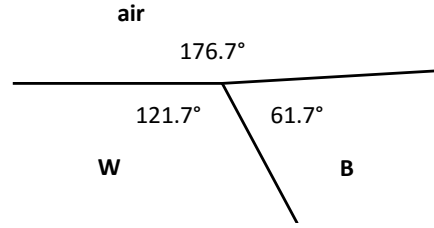

Figure 2. The equilibrium angles for water-saturated butanol (B), butanol-saturated water (W) and air, at 296 K.
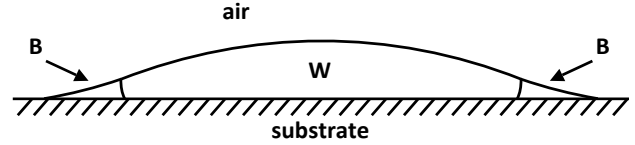

Figure 3. A physical model of the arrangement of phases were water-saturated butanol (B) to separate from butanol-saturated water (W) at the contact line. The model is based on measured surface and interfacial tensions (T = 296 K) and contact angles on a hydrophobized substrate (T = 295 K).

$$\Delta p = \frac{2\gamma}{R}, \tag{6}$$

where Δp is the difference in pressure on either side of an interface and R is the radius of curvature. The sign of the curvature is determined when passing from the phase indicated by the first superscript to the second. For a particular phase, the Laplace pressure must be equal at all interfaces and, since each of the phases in Figure 2 is in contact with both of the other two, the Laplace pressure of each phase must be the same. The following equality must then hold:

$$-\frac{\gamma^{\rm OA}_{\rm sat}}{R^{\rm OA}_{\rm sat}} = \frac{\gamma^{\rm WA}_{\rm sat}}{R^{\rm WA}_{\rm sat}} = \frac{\gamma^{\rm WA}_{\rm sat}}{R^{\rm WA}_{\rm sat}}. \tag{7}$$

The ratio between the three radii of curvature, $R^{\rm OA}_{\rm sat} : R^{\rm WA}_{\rm sat} : R^{\rm WO}_{\rm sat}$, is $-14.6 : 15.1 : 1.0$ and would appear as in Figure 3. Both of the boundaries along the butanol-rich phase are concave, allowing the sum of the three internal angles to sum to less than 180°, whilst both of the boundaries along the water-rich phase are convex. The arrangement in Figure 3 shows that the butanol-rich phase would not undercut the water-rich phase completely.

When a 6 %wt butanol solution was printed onto a hydrophobized substrate, however, no phase separation was observed. The formulation had been seeded with 0.05 %wt polystyrene particles of diameter 1 μm, which reveal the presence and directionality of any internal flows during the drying process. After deposition, a flow is initially present that moves radially inwards along the base of the drop and along the liquid-air surface from the apex to the contact line (Fig. 4). This behavior is a Marangoni flow and is indicative of a surface tension gradient along the liquid-air surface [3], [10]. The direction of movement of the particles shows that the drop apex has a lower surface tension than the contact line, such that fluid is "pulled" from the former to the latter [3]. For an aqueous butanol solution, the surface tension increases towards the pure value for water as the concentration of the solute decreases. The printed drop is therefore deficient in butanol at the contact line relative to the apex and the local concentration of butanol is determined by the evaporative flux profile (Fig. 4). Butanol is
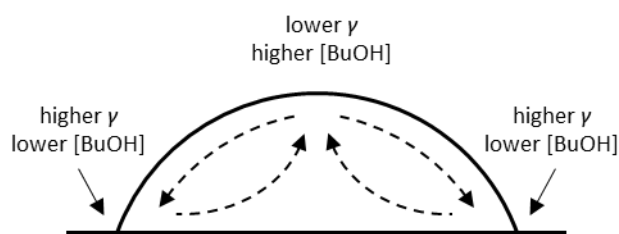
Figure 4. The internal flows observed in an evaporating drop of a 6 %wt butanol solution.
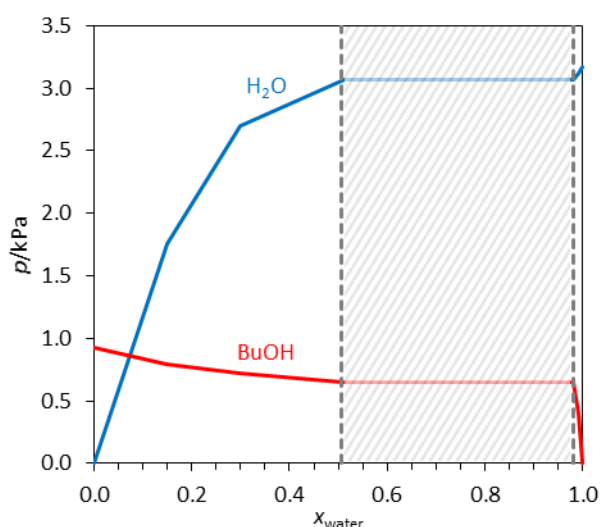

Figure 5. The vapor pressures p of water (blue) and butanol (red) in binary solution, as a function of the mole fraction of water, x_{water} at 298 K. Data from Reference [11]. The shaded area between the dashed grey lines represents the two-phase region.
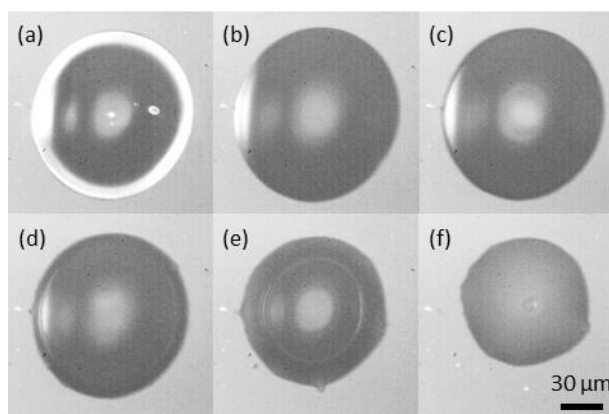

Figure 6. A drop of 15.1 %wt DPGMEA solution as viewed from underneath. Images were captured (a) 8 ms, (b) 0.20 s, (c) 0.40 s, (d) 0.80 s, (e) 1.60 s and (f) 3.00 s after deposition. The drop was jetted with a symmetrical bipolar waveform with a drive voltage of 30 V.
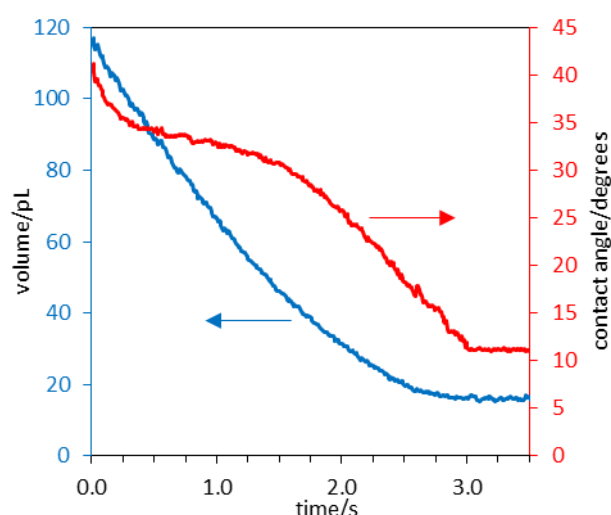

Figure 7. The drop volume (blue) and contact angle (red) of a 15.1 %wt DPGMEA solution over time. The drop was jetted with a symmetrical bipolar waveform with a drive voltage of 30 V.

therefore evaporating too quickly for phase separation to be observed. After 1.86 s, the Marangoni flows ceased and the particles began an outward radial migration, commonly referred to as coffee-ring flow [2], indicating that the surface tension had become uniform across the surface and that the drop now only possesses one component: water. A second phase, rich in butanol, is not able to form if the lifetime of the minor component is shorter than the lifetime of the major component.

The origin of the failure of a saturated solution of butanol to phase separate under ink-jet printing conditions is the non-ideality of the component vapor pressures. The component vapor pressures do not obey Raoult's law and show significant deviations (Fig. 5). The binary solution does not exist at all concentrations with the water-rich phase having a minimum $x_{water} = 0.98$ and the butanol-rich phase having a maximum $x_{water} = 0.51$ [8]. At intermediate compositions the two phases coexist at equilibrium and, consequently, each component must have the same vapor pressure in both phases. The vapor pressure deviates strongly from proportionality with the mole fraction and is independent through the two-phase region. The vapor pressure of butanol in aqueous solution is better described by Henry's law

$$p_A = x_A H_A, \tag{8}$$

where H_A is the Henry constant, which is defined as the limiting value of p_A as x_A tends to zero. The Henry constant for butanol in water at 298 K is 44.8 kPa [5] and, as Henry law

behavior is observed up to saturation (Fig. 5), its vapor pressure in the saturated solution is 0.90 kPa. The vapor pressure of butanol is therefore comparable to the pure liquid value of 0.93 kPa [5] and 50 times higher than would be expected if the solution were ideal. The vapor pressure of water in a saturated butanol solution is 3.1 kPa, barely deviating from the pure liquid value [11]. Using the Henry law vapor pressure for butanol, taking the vapor pressure of water to be unchanged from the pure liquid value and $RH = 0.4$, $\kappa^{henry} = 0.08$. A value less than unity indicates phase separation will not be observed. Though butanol is less evaporative than water, it is not present in a sufficient quantity to outlast the water. A saturated solution of butanol in water cannot phase separate because if a second phase were to form, it would evaporate quickly relative to the water-rich phase. The value of κ^{henry} is a good indicator of whether phase separation is expected and explains the behavior of aqueous butanol solutions well. In general, where the value of the Henry constant is not readily available for a solute in a particular solvent, the pure liquid vapor pressures may be used as an estimate of the partial vapor pressure in the saturated mixtures. In the case of water and butanol, this approximation would make barely perturb the value of κ.

TABLE 1. Physical data at 298 K relating to a series of potential components for formulating aqueous phase-separating fluids under evaporation and an assessment of their viability.

A	Solubility/%wt[a]	$x_{A,lim}$	H_A/kPa[b]	$p_{A,lim}$/kPa	D_A/(cm^2/s)[c]	κ^{henry}	Viable?
1 *n*-Butanol	7.5	0.0192	44.8	0.862	0.090	0.08	N
2 Acetic Anhydride	15.0	0.0300	24.2	0.726	0.086	0.16	N
3 Isobutyric Acid	20.0	0.0486	4.96	0.241	0.087	0.77	N
4 Furfural	7.9	0.0158	18.2	0.289	0.089	0.20	N
5 Acetylacetone	10.0	0.0196	25.3	0.497	0.081	0.16	N
6 Aniline	3.4	0.0068	9.52	0.064	0.085	0.39	N
7 Cyclohexanol	3.8	0.0071	14.2	0.100	0.081	0.28	N
8 Isovaleric Acid	4.1	0.0075	7.90	0.059	0.079	0.51	N
9 Valeric Acid	2.4	0.0043	7.50	0.032	0.079	0.54	N
10 *m*-Cresol	2.2	0.0037	4.06	0.015	0.078	1.01	N
11 Butyl Acetate	0.7	0.0011	2347	2.490	0.073	0.002	N
12 Propylene Glycol Methyl Ether Acetate	16.0	0.0253	24.1	0.609	0.070	0.19	N
13 Dipropylene Glycol Methyl Ether Acetate	16.0	0.0177	1.16	0.021	0.057	4.86	Y
14 Dipropylene Glycol *n*-Propyl Ether	19.6	0.0243	1.15	0.028	0.058	4.91	Y
15 Propylene Glycol *n*-Butyl Ether	5.5	0.0079	22.0	0.173	0.066	0.22	N
16 Dipropylene Glycol *n*-Butyl Ether	4.5	0.0044	2.16	0.010	0.055	2.69	Y
17 Tripropylene Glycol *n*-Butyl Ether	4.5	0.0034	0.23	0.001	0.048	28.7	Y
18 Propylene Glycol Phenyl Ether	1.0	0.0012	2.55	0.003	0.065	1.91	Y
19 Propylene Glycol Diacetate	7.4	0.0089	0.80	0.007	0.065	6.12	Y
20 Dipropylene Glycol Dimethyl Ether	35.0	0.0564	0.07	0.004	0.061	77.3	Y
21 Diethylene Glycol Hexyl Ether	2.0	0.0019	0.10	0.0002	0.055	59.5	Y
22 Diethylene Glycol *n*-Butyl Ether Acetate	4.0	0.0037	0.20	0.001	0.055	29.0	Y
23 Ethylene Glycol *n*-Butyl Ether Acetate	1.6	0.0018	31.3	0.057	0.062	0.16	N
24 Ethylene Glycol Phenyl Ether	2.5	0.0033	1.14	0.004	0.066	4.24	Y

[a] [1−11] Ref [5], [12−24] Ref [6]; [b] [1−10] Ref [5], [11, 19, 21−23] Ref [12], [12−18, 20, 24] Ref [13]; [c] [1−24] Ref [9].

A binary solution that would phase separate upon printing will have $\kappa^{henry} > 1$. In order to isolate a mixture that will phase separate, a wide series of liquids that have partial miscibility with water at room temperatures have been screened using this criterion and recorded in Table 1. Water has been assumed to have a negligible change in vapor pressure in the mixtures, as was the case for butanol solutions. The search focused on materials that have an aqueous solubility of the same order as butanol, so that any phase that separated out would have an appreciable volume. The value of H_A was then considered, with better candidates having a value lower than that of butanol. None of candidates 1−11 will produce aqueous formulations that phase separate under printing conditions because $\kappa^{henry} < 1$. They have the correct solubility characteristics but their vapor pressure in solution at the solubility limit is too high. *m*-Cresol is borderline but is excluded from further investigation on account of its toxicity. The remaining entries in Table 1 (12−24) are glycol ether derivatives, which provide more viable candidates for components of phase-separating formulations under evaporation. The increased molecular size has the dual effect of lowering the vapor pressure at ambient temperatures and lowering D_A so that some have $\kappa^{henry} > 1$. The great majority of the glycol ethers tabulated are expected to supersaturate

during the evaporation of a binary aqueous solution. Some of them, however, have such low vapor pressures that complete evaporation would not be achieved on a practical timescale. Dipropylene glycol methyl ether acetate and dipropylene glycol *n*-propyl ether have the highest vapor pressures of the viable glycol ether candidates and thus appear to be the most suitable.

An aqueous 15.1 %wt DPGMEA solution is close to the miscibility limit and printing trials were conducted with this solution. In contrast to the butanol solution, the DPGMEA solution did phase separate upon deposition onto the substrate. Figure 6 displays images of the drying process as viewed from underneath and Figure 7 shows the change volume and contact angle over time. The drop initially forms a spherical cap on the substrate and is a single phase (Fig. 6a). Over the first 0.2 s of drying time the contact line remains pinned and the volume loss is reflected in the decreasing contact angle. At *t* = 0.4 s, rate of contact angle decrease becomes smaller, coinciding with the appearance of a second phase at the contact line (Fig. 6c). The phase boundary moves radially inwards (Figs. 6d and e) until *t* = 3.0 s, when only one phase remains (Fig. 6f) and the volume and contact angle become constant. The volume of the liquid remaining after *t* = 3.0 s is 16 pL out of the initial 115 pL, representing 14% of the original volume, matching the initial

proportion of DPGMEA (ρ = 0.97 g/ml) present in the formulation. DPGMEA has therefore increased in concentration at the contact line due to relatively rapid water evaporation and the local composition has passed through the binodal, leading to phase separation. The phase boundary has then moved inwards as more water evaporates until only DPGMEA remains on the substrate.

Conclusion

In this paper we presented an exploratory investigation into ink-jet formulations that phase separate upon deposition onto the substrate. Aqueous solutions of butanol and dipropylene glycol methyl ether acetate (DPGMEA) were ink-jet printed onto hydrophobized substrates and images of the drying process were captured using high-speed cameras viewing the droplets from below and in profile. A physical model of how the butanol-rich phase would have been expected to behave should separation be observed was constructed. The prediction was based on measured surface and interfacial tensions and contact angles. The results showed that an annular ring of the butanol-rich phase would undercut the water-rich phase slightly. The saturated butanol solution did not, however, show any evidence of phase separation. Marangoni flows inside the drops circulated radially inwards along the base of the drop and from the apex to the contact line. Butanol therefore evaporated preferentially at the contact line and had a shorter lifetime on the substrate than water. In contrast, the DPGMEA solution did phase separate. A printed droplet showed a decrease in the rate of contact angle reduction when a second phase appeared as an annular ring around the contact line. The phase boundary moved radially inwards over time until water evaporation was complete and a volume reflecting the initial ether acetate proportion in the formulation was left.

Analysis of the component vapor pressures was key to understanding the difference in behavior for the butanol and DPGMEA solutions. Assuming that butanol and water in a binary solution have ideal vapor pressures incorrectly leads one to predict the solution would phase separate. The vapor pressure of butanol deviates strongly from ideality at low concentrations and is 50 times higher than might otherwise be expected. The result is that the minor component is not present in sufficient quantity to remain on the substrate longer than the major. A criterion for the observation of phase separation on the substrate based on the Henry law vapor pressure for the solute was presented. The criterion was used to screen a variety of aqueous systems in order to find some phase-separating candidates. Glycol ethers in aqueous solution were found to be excellent candidates since they have appreciable solubility but low vapor pressures and diffusion coefficients.

Acknowledgements

References

[1] S. D. Hoath, Ed., *Fundamentals of Inkjet Printing: The Science of Inkjet and Droplets*. Weinheim, Germany: Wiley-VCH, 2016.

[2] R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel, and T. A. Witten, "Capillary flow as the cause of ring stains from dried liquid drops," *Nature*, vol. 389, no. 6653, pp. 827–829, 1997.

[3] T. Still, P. J. Yunker, and A. G. Yodh, "Surfactant-Induced Marangoni Eddies Alter the Coffee-Rings of Evaporating Colloidal Drops," *Langmuir*, vol. 28, no. 11, pp. 4984–4988, 2012.

[4] E. L. Talbot, L. Yang, A. Berson, and C. D. Bain, "Control of the Particle Distribution in Inkjet Printing through an Evaporation-Driven Sol-Gel Transition," *ACS Appl. Mater. Interfaces*, vol. 6, no. 12, pp. 9572–9583, 2014.

[5] C. L. Yaws, Ed., *Chemical Properties Handbook: Physical, Thermodynamic, Environmental, Transport, Safety, and Health Related Properties for Organic and Inorganic Chemicals*. New York, U.S.A.: McGraw-Hill, 1999.

[6] *Product Information: DOW P-Series Glycol Ethers and DOW E-Series Glycol Ethers*. DOW Chemical.

[7] H. Hu and R. G. Larson, "Evaporation of a Sessile Droplet on a Substrate," *J. Phys. Chem. B*, vol. 106, no. 6, pp. 1334–1344, 2002.

[8] M. Góral, B. Wiśniewska-Gocłowska, and A. Mączyński, "Recommended Liquid–Liquid Equilibrium Data. Part 4. 1-Alkanol–Water Systems," *J. Phys. Chem. Ref. Data*, vol. 35, no. 3, pp. 1391–1414, 2006.

[9] E. N. Fuller, K. Ensley, and J. C. Giddings, "Diffusion of Halogenated Hydrocarbons in Helium. The Effect of Structure on Collision Cross Sections," *J. Phys. Chem.*, vol. 73, no. 11, pp. 3679–3685, 1969.

[10] J. Park and J. Moon, "Control of Colloidal Particle Deposit Patterns within Picoliter Droplets Ejected by Ink-Jet Printing," *Langmuir*, vol. 22, no. 8, pp. 3506–3513, 2006.

[11] J. A. V. Butler, D. W. Thomson, and W. H. Maclennan, "The free energy of the normal aliphatic alcohols in aqueous solution. Part I. The partial vapour pressures of aqueous solutions of methyl, n-propyl, and n-butyl alcohols. Part II. The solubilities of some normal aliphatic alcohols in water. Part III. The ," *J. Chem. Soc.*, pp. 674–686, 1933.

[12] R. Sander, "Compilation of Henry's law constants (version 4.0) for water as solvent," *Atmos. Chem. Phys.*, vol. 15, no. 8, pp. 4399–4981, 2015.

[13] *Product Information: Ecological and Toxicological Data of DOW Glycol Ethers*. Dow Chemical.

Author Biography

Ashley Johns was awarded Master of Chemistry by the University of Durham (United Kingdom) in 2013. He is presently a PhD candidate at the same institution under the supervision of Prof. C. D. Bain. His work is focused on ink-jet printing complex ink-jet formulations and investigating the drying dynamics of drops on the substrate.