



Relationship between the dye/additive interaction and inkjet ink droplet formation

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ABSTRACT

To design adequate ink composition for textile printing, the relationship between the dye/additive interaction and ink performance is investigated. In the present study, the three acid dyes C. I. Acid Red 88, 13, and 27, a water-soluble polymer poly(vinylpyrrolidone) (PVP) and three surfactants, sodium dodecyl sulfate (SDS), octaethylene glycol monododecyl ether (OGDE), and Surfynol 465 (S465) were used and the dye/additive interaction was investigated by means of visible absorption measurements. The visible absorption spectra of aqueous dye solutions changed with the addition of the nonionic surfactants, but further addition of PVP had little effect on the spectra, indicating that the strong binding of the dye molecules with the nonionic surfactant micelles is maintained even in the presence of PVP. In contrast, in the case of SDS, the spectra changed with the addition of the surfactant as well as with further addition of PVP. This indicates that the behavior of the acid dyes in the three-species system depends on the dye structure, the surfactant structure, and the molecular weight of PVP. Furthermore, to estimate the ink performance, the physical properties of the ink, such as viscosity, surface tension, and ink droplet formation were determined. Ink solutions with favorable physicochemical properties and low molecular weight PVP showed good ink droplet formation. In the optimized ink composition (PVP-1/S465: 1.4/0.004 mol dm⁻³) most of the dye molecules are strongly bound to the PVP chain, but the binding is not significantly affected by the addition of S465.

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1. Introduction

Inkjet ink contains not only dyes or pigments but also additives, and the types and amounts of the additives are the most important factors for designing adequate ink composition for textile printing. Various types of additives, such as surfactants, polymers, and inorganic salts are used to adjust the physical properties of the ink [1–4], and improve the fastness properties [5–8], image quality [9–11], ink durability [4,12], and ink penetration [4,5,8,9,13].

In the inkjet ink, dye–dye, dye–additive and additive–additive interactions are observed. There have been numerous studies on dye aggregation [14–21], dye/polymer interactions [22–28], dye/surfactant interactions [29–34], polymer/surfactant interactions [35–39], and dye/polymer/surfactant interactions [40–43]. However, there have been no studies on the relationship between the dye/additive interaction and ink droplet formation.

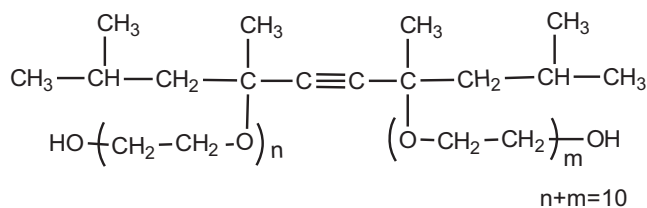
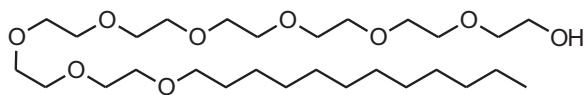
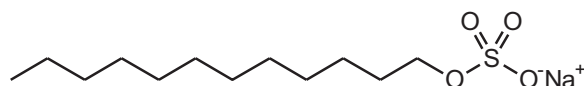
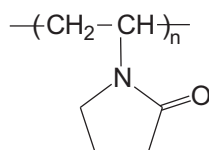
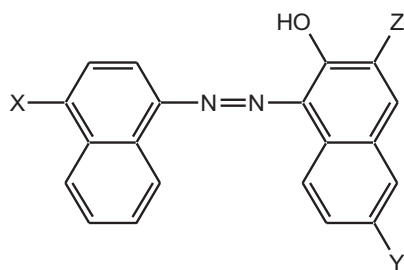
In a previous study we investigated the dye–dye interaction, *i.e.*, the aggregation behavior of three acid dyes (C. I. Acid Red 88, 13,

and 27) containing different numbers of sulfonate groups [44]. We found that the higher the solubility of the dyes in water, the lower the aggregation constants of the dyes. The dye–additive interactions, *i.e.* the interaction of the acid dyes with a water-soluble polymer additive, of poly(vinylpyrrolidone) (PVP) and surfactant micelles have also been investigated [45,46]. It was found that the higher the solubility of the acid dyes in water (the larger the number of sulfonate groups in the dyes), the lower the binding affinity of PVP to the surfactant micelles, indicating that the hydrophobic interaction is important in the binding processes. Furthermore, the binding constants of the dyes with PVP decreased with increasing molecular weight of PVP [45]. The binding constants for the nonionic surfactants octaethylene glycol monododecyl ether (OGDE) and Surfynol 465 (S465) are much larger than those for the anionic surfactant sodium dodecyl sulfate (SDS), suggesting that electrostatic repulsion between the negatively charged groups of the dyes and SDS decreases the affinity [46]. From the above results, it can be concluded that the binding affinities are influenced by the dye structure, the polymer molecular weight, the surfactant structure, and the micelle shape.

The physicochemical properties of ink for textile printing should be optimized for the specific inkjet technology, the print heads, and

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**S465****OGDE****SDS****PVP**

- R-1:** X = SO₃Na, Y = H, Z = H
R-2: X = SO₃Na, Y = SO₃Na, Z = H
R-3: X = SO₃Na, Y = SO₃Na, Z = SO₃Na

Dyes**Fig. 1.** Chemical structure of the surfactants, PVP and the acid dyes.

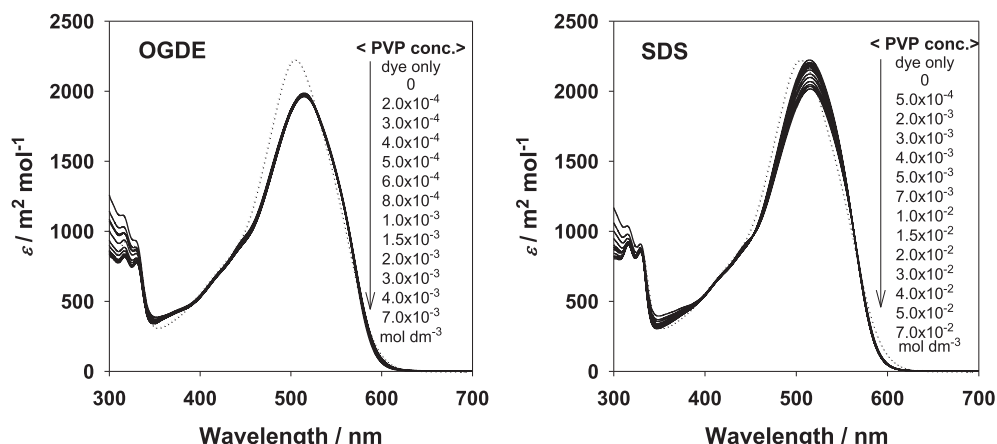
the printing device [1,4,11,47–49]. The main parameters that govern the ejection process of inkjet printing are the surface tension, the viscosity, and the rheological properties of the ink. The rheology of ink is an extremely important parameter because it aids droplet formation through the nozzle in a controlled manner for any given inkjet technology [50]. Droplet formation affects the overall performance of the printing process. Inkjet printing quality depends on the velocity and shape fluctuations of the jet and drops, as well as on the existence of satellite drops [51]. These ejection properties are greatly affected by the viscosity and surface tension of the ink [1,12]. For adequate droplet formation, the viscosity of the ink should be kept low to obtain good jetting properties [52] and the surface tension must also be low enough so that the ink wets the capillary channels and flows through the nozzle [1]. Although the physical properties depend on the print head and ejection conditions, typical inkjet ink should have a surface tension of 25–50 mN m^{−1} and a viscosity of 1–25 mPa s [53]. To prepare ink with adequate viscosity and surface tension, polymers are used to control the viscosity and surfactants are added to control the surface tension [53].

In this study, to elucidate the interaction between dyes and additives the behavior of three acid dyes (C. I. Acid Red 88, 13, and 27) in aqueous solutions containing both a water-soluble polymer, poly(vinylpyrrolidone) (PVP) and a surfactant (sodium dodecyl sulfate (SDS), octaethylene glycol monododecyl ether (OGDE), or Surfynol 465 (S465)) were investigated by means of visible absorption measurements. The effect of PVP concentration in aqueous solutions containing constant concentrations of the dyes and the surfactants, as well as the influence of the surfactant concentration in aqueous solutions containing constant concentrations of the dyes and PVP have been investigated. Furthermore, the physical properties of the ink, such as viscosity, surface tension, and the ink droplet formation were determined. We focus on the effects of polymer molecular weight on the ink droplet formation and analyzed the experimental results by the physicochemical properties of ink compositions and droplet forming. From these results, the relationship between the dye/additive interactions and ink droplet formation is discussed.

2. Experimental

2.1. Materials

Three acid dyes containing different numbers of sulfonate groups, C. I. Acid Red 88 (R-1), C. I. Acid Red 13 (R-2), and C. I. Acid Red 27 (R-3) were used (Fig. 1). R-1 and R-3 were purchased

**Fig. 2.** Visible absorption spectral change of aqueous R-1 solutions with PVP-1 concentration in presence of the surfactants at 25 °C (OGDE; 0.006, SDS; 0.05 mol dm^{−3}).

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