



# 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<sup>-3</sup>) 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.

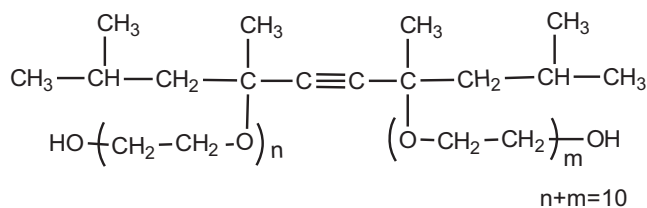
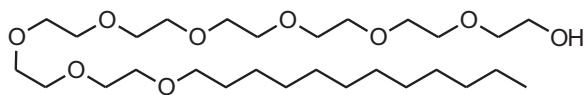
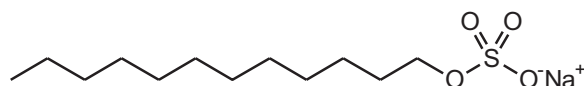
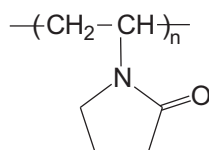
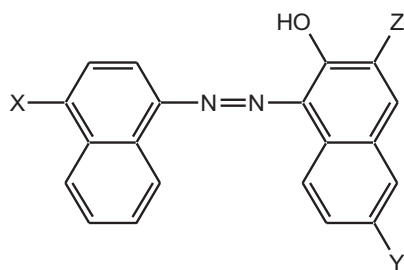
In a previous study we investigated the dye–dye interaction, *i.e.*, the aggregation behavior of three acid dyes (C. I. Acid Red 88, 13,

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 = SO<sub>3</sub>Na, Y = H, Z = H  
**R-2:** X = SO<sub>3</sub>Na, Y = SO<sub>3</sub>Na, Z = H  
**R-3:** X = SO<sub>3</sub>Na, Y = SO<sub>3</sub>Na, Z = SO<sub>3</sub>Na

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

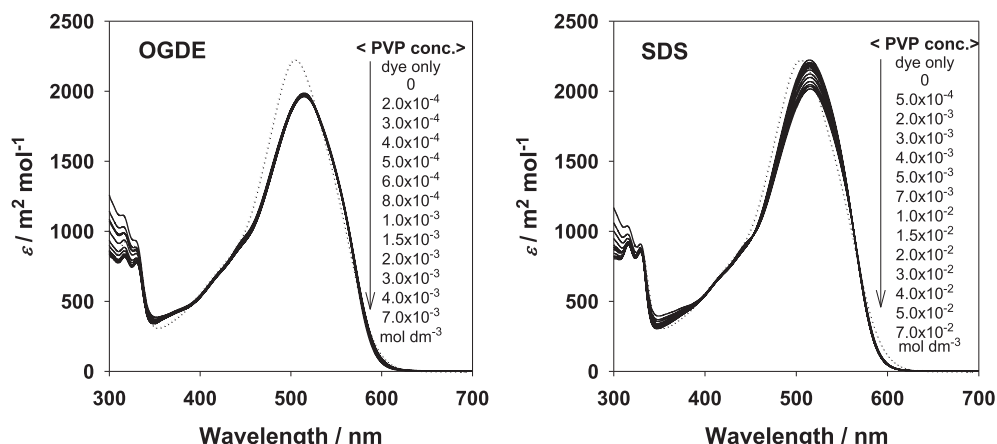
the printing device [1,4,11,47–49]. The main parameters that govern the ejection process of inkjet printing are the surface tension, the viscosity, and the rheological properties of the ink. The rheology of ink is an extremely important parameter because it aids droplet formation through the nozzle in 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<sup>−1</sup> 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].

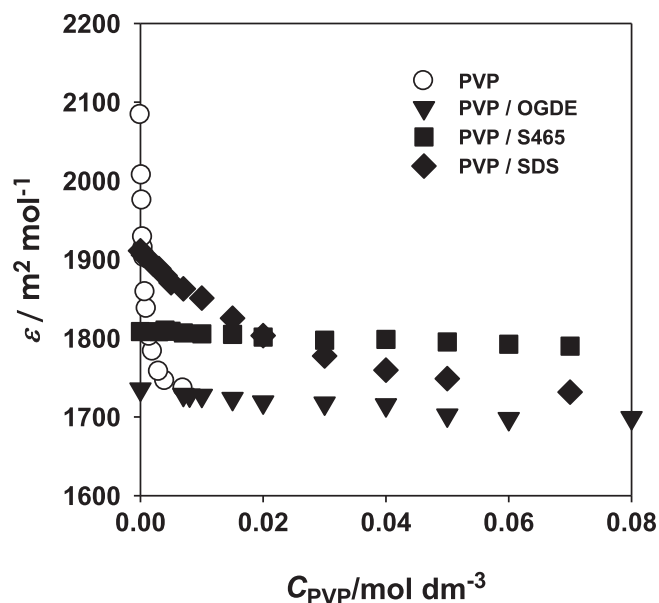
In this study, to elucidate the interaction between dyes and additives the behavior of three acid dyes (C. I. Acid Red 88, 13, and 27) in aqueous solutions containing both a water-soluble polymer, poly(vinylpyrrolidone) (PVP) and a surfactant (sodium dodecyl sulfate (SDS), octaethylene glycol monododecyl 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<sup>−3</sup>).



**Fig. 3.** Dependence of the extinction coefficients on PVP-1 concentration for R-1 in the absence and presence of the surfactants at 25 °C and 492 nm (OGDE; 0.006, S465; 0.02, SDS; 0.05  $\text{mol dm}^{-3}$ ).

from Tokyo Chemical Industry Co., Ltd., and used after purification. R-2 was prepared by coupling diazotized 4-amino-1-naphthalenesulfonic acid with sodium 2-hydroxy-6-naphthalene-sulfonate under alkaline conditions and purified as described in a previous paper [44].

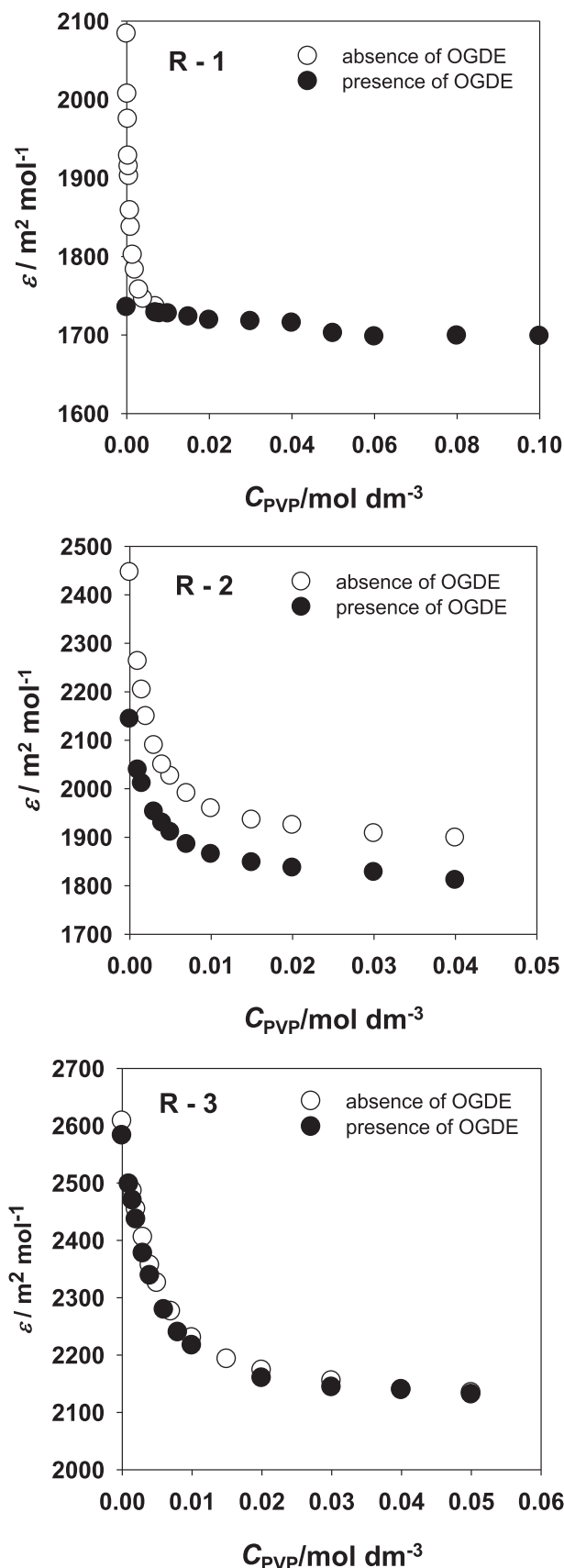
As polymer additives, three types of PVP with different molecular weight (Mw) (PVP-1, Mw ~10,000; PVP-4, Mw ~40,000; and PVP-63, Mw ~630,000) were used (Fig. 1). All of the polymers were purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification.

As the surfactant, the nonionic gemini surfactant Surfynol 465 (S465,  $\alpha, \alpha'$ -[2,4,7,9-tetramethyl-5-decyne-4,7-diyl]bis[ $\omega$ -hydroxypoly(oxyethylene)]), with a total of 10 oxyethylene segments, the nonionic surfactant octaethylene glycol monododecyl ether (OGDE), and the anionic surfactant sodium dodecyl sulfate (SDS) were used (Fig. 1). S465 was supplied by Air-Product and Chemicals Inc. and was used without further purification. OGDE and SDS were purchased from Wako Pure Chemical Industries Ltd. and used without further purification.

## 2.2. Methods

### 2.2.1. Visible absorption spectroscopy

The visible absorption spectra of aqueous solutions with various PVP concentrations, a constant dye concentration (R-1;  $2.97 \times 10^{-5} \text{ mol dm}^{-3}$ ), and constant surfactant concentrations above the critical micelle concentration (cmc) (OGDE, 0.006  $\text{mol dm}^{-3}$ ; S465, 0.02  $\text{mol dm}^{-3}$ ; and SDS, 0.05  $\text{mol dm}^{-3}$ ) were measured using a JASCO UV-530 spectrophotometer at 25 °C. The visible absorption spectra of aqueous solutions with various surfactant concentrations and constant dye concentrations (R-1,  $2.97 \times 10^{-5} \text{ mol dm}^{-3}$ ; R-2,  $2.81 \times 10^{-5} \text{ mol dm}^{-3}$ ; and R-3,  $2.83 \times 10^{-5} \text{ mol dm}^{-3}$ ) were measured in the absence and presence of 0.1  $\text{mol dm}^{-3}$  PVP, where PVP concentration is based on the monomer unit. In addition, to investigate the dye/additive interaction in the ink solutions containing the dye, surfactants, and polymers, visible absorption spectra were measured using a JASCO UV-530 spectrophotometer at 25 °C.



**Fig. 4.** Dependence of the extinction coefficients on PVP-1 concentration for three acid dyes in the absence and presence of OGDE (0.006  $\text{mol dm}^{-3}$ ) at 25 °C and 492 nm.

### 2.2.2. Ink preparation

From the viewpoint of the discharge property of the inkjet head, a viscosity of 3–4 mPa s and a surface tension of 33–36 mN m<sup>-1</sup> at 25 °C are desirable in the present study. To obtain adequate viscosity, the concentrations of the polymers used were 1.4, 0.7, and 0.135 mol dm<sup>-3</sup> for PVP-1, PVP-4, and PVP-63, respectively. To obtain adequate surface tension, the surfactant (S465) concentrations used were in the range of 0–0.01 mol dm<sup>-3</sup>. The dye concentration used was  $2.97 \times 10^{-5}$  mol dm<sup>-3</sup>.

### 2.2.3. Viscosity and surface tension measurements

The viscosity of the ink solutions was measured using a sine-wave vibro viscometer (SV-10, A&D Company Limited, Japan) at 25 °C. This viscometer consists of two sensor plates that vibrate at a constant frequency of 30 Hz, which gives a constant shear rate. A Wilhelmy balance surface tensiometer (CBVP-A1, Kyowa Interface Co., Japan) equipped with a platinum plate was used to measure the surface tension of the inks at 25 °C.

### 2.2.4. Droplet formation measurements

The formation of ink droplets was measured by a JetLyzer (Mimaki Engineering Co. Ltd. Ver. T-0.782) equipped with a CA4 inkjet print head (Toshiba Tec. Corporation). The droplet firing conditions used were a discharge voltage of 22 V, a pulse width of 1.00 μs, a channel pitch of 169 μm, and a discharge drop number of 5 drops (drop on demand (DOD), piezo method).

## 3. Results and discussions

### 3.1. Behavior of the acid dyes in aqueous solutions containing PVP and surfactant

#### 3.1.1. Effect of PVP concentration

The change in the visible absorption spectra of aqueous R-1 solutions with PVP-1 concentration in the presence of the surfactants is shown in Fig. 2. The maximum absorption wavelength shifted to a higher wavelength (red shift) with the addition of the surfactants. Addition of the nonionic surfactant OGDE changed the spectra, but further addition of PVP had little effect. A similar change was observed for the nonionic gemini surfactant S465. In contrast, for the anionic surfactant SDS, the spectra changed with the addition of the surfactant as well as further addition of PVP.

To analyze the spectral change with PVP concentration, the extinction coefficients ( $\epsilon$ ) at the wavelength where the largest

difference was observed (492 nm) was used. The change of the extinction coefficients with increasing polymer concentration in the absence and presence of the surfactants is shown in Fig. 3. In the presence of OGDE and S465, the extinction coefficients did not significantly change with increasing PVP concentration. This means that the strong binding of the dye molecule with the nonionic surfactant micelles is maintained even in the presence of PVP. In contrast, for the anionic surfactant SDS the extinction coefficients decreased with increasing PVP concentration, indicating that the dyes bind to PVP. This result might be due to the fact that PVP influences the behavior of SDS micelles and the dye prefers to bind with PVP rather than the SDS micelles.

In our previous study [46], the binding affinity of the dyes with the micelles was highly dependent on the aqueous solubility of the acid dyes, in particular for the case of OGDE (binding constants of the dyes with OGDE micelles: R-1, not determined but considerably greater than R-2; R-2,  $260000 \text{ dm}^3 \text{ mol}^{-1}$ ; R-3,  $3200 \text{ dm}^3 \text{ mol}^{-1}$ ). To discuss the effect of the dye structure in aqueous solutions containing the three species in more detail, the change of the extinction coefficients with PVP-1 concentration was investigated for three acid dyes having a different number of the sulfonate groups (Fig. 4). In the absence of PVP (see the ordinate axis in Fig. 4), the extinction coefficients decreased with the addition of OGDE. The magnitude of the decrease was in the order  $R-3 < R-2 < R-1$ , which corresponds to the increasing order of the affinity of the dyes for the surfactant micelles ( $R-3 < R-2 < R-1$ ) determined in a previous study [46]. The magnitude of the change in the extinction coefficients with PVP concentration was different for the three dyes. In the case of R-1/OGDE, the extinction coefficients did not significantly change with increasing PVP concentration. This suggests that the R-1 molecules are incorporated into the OGDE micelles and the R-1 molecules cannot bind with the PVP chains. The extinction coefficients for the ternary systems (R-2/OGDE/PVP) were smaller than those for the binary systems (R-2/PVP) in the polymer concentration region investigated, suggesting that all R-2 molecules are not incorporated into the micelles and the remaining free dye can bind to the PVP chains. In the case of aqueous R-3 solutions, the presence of OGDE did not influence the extinction coefficients with increasing PVP concentration. This suggests that the R-3 molecules are not incorporated into the OGDE micelles, owing to their high water solubility. In the R-2/OGDE and R-3/OGDE solutions, the anionic groups of the remaining free dye may bind with the positively charged pyrrolidone rings, because the pyrrolidone rings of PVP can be protonated in aqueous solutions, as described in

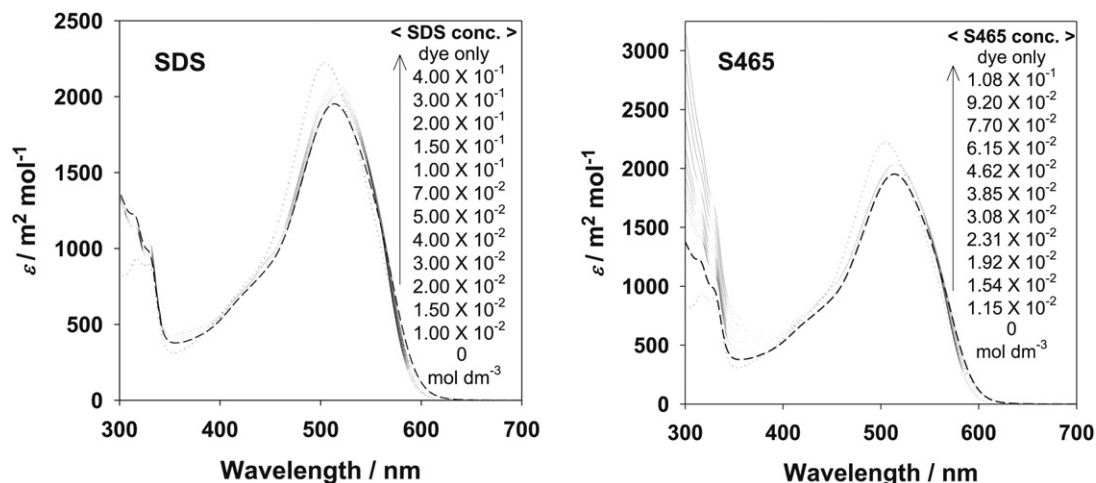


Fig. 5. Visible absorption spectra change of aqueous R-1 solutions with SDS and S465 concentration in presence of PVP ( $0.1 \text{ mol dm}^{-3}$ ) at 25 °C.

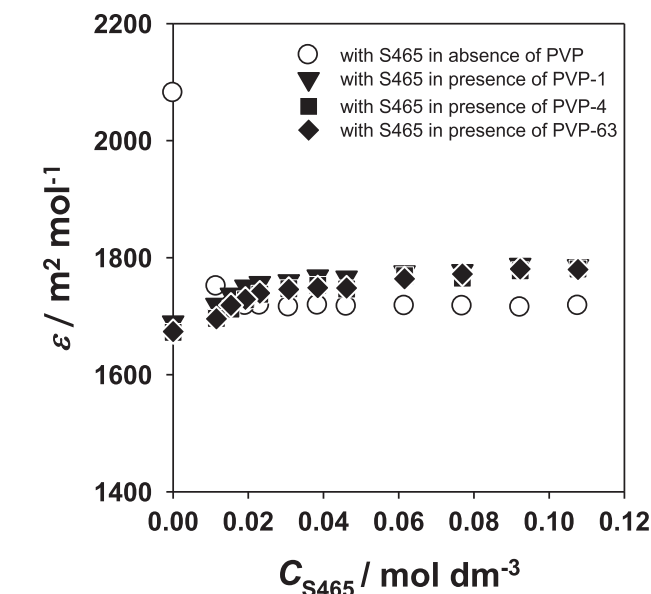
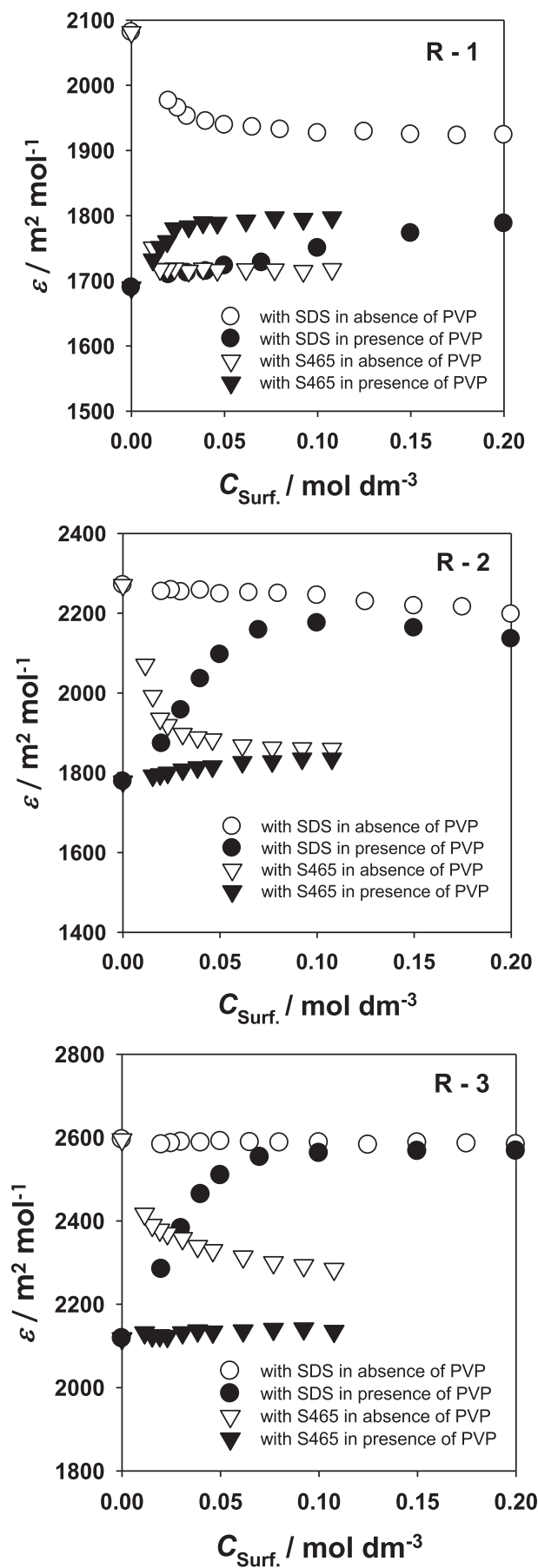


Fig. 7. Dependence of the extinction coefficients on S465 concentration for R-1 in the absence and presence of three kinds of PVP's ( $0.1 \text{ mol dm}^{-3}$ ) with different molecular weights at  $25^\circ\text{C}$  and  $492 \text{ nm}$ .

previous studies [24,27,45]. From the above results, the binding affinity of the dyes with the OGDE micelles affects the interaction between the dyes and PVP: the higher the affinity for the surfactant micelles, the lower the binding force with PVP.

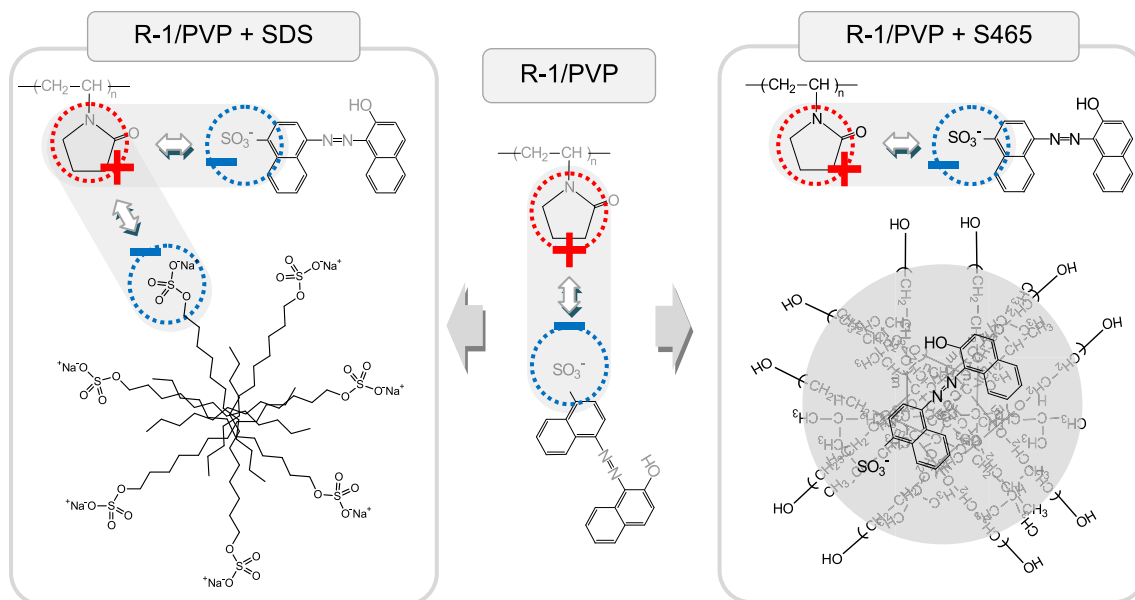
### 3.1.2. Effect of the surfactant concentration

Fig. 5 shows the effect of surfactant concentration on the visible absorption spectra of R-1 in the presence of PVP-1. The maximum absorption wavelength for the aqueous R-1 solutions shifted to a higher wavelength (red shift) and the extinction coefficient at that wavelength decreased with the addition of PVP. Further addition of the surfactants increased the extinction coefficients. A similar spectral change was observed for R-2 and R-3. This suggests that the surfactants hinder the binding of the dye to PVP, leading to the incorporation of the dyes in the surfactant micelles. Furthermore, the spectral change when increasing the surfactant concentration for aqueous R-1/PVP/SDS solutions was larger than for aqueous R-1/PVP/S465 solutions, which indicates that PVP binds to SDS but not to S465. This result is in agreement with a previous study [37], in which the association of anionic surfactant to a hydrophilic homopolymer was found to be strongly cooperative, whereas a nonionic surfactant shows only weak interaction with most homopolymers. The addition of SDS causes unfolding of the PVP chains [54] and SDS interacts more closely with the positively charged pyrrolidone rings of PVP.

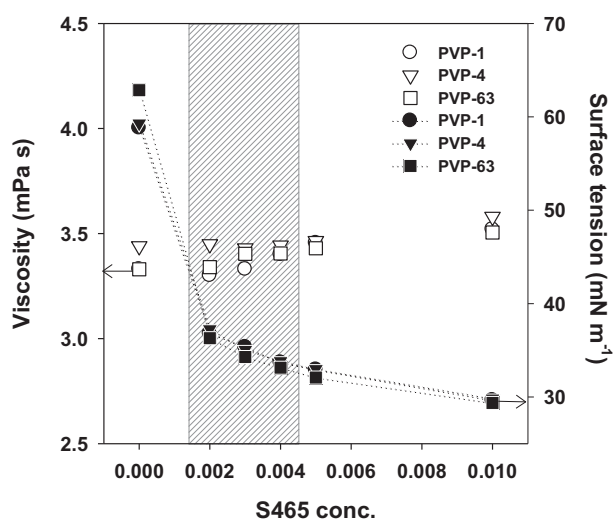
The relative efficacy of the surfactant concentrations on the extinction coefficients in the aqueous solutions containing the dyes and PVP is shown in Fig. 6. In the absence of PVP, the change in the extinction coefficients for the aqueous S465 solutions was larger than for the aqueous SDS solutions, indicating that the acid dye is bound to the S465 micelle but not to the SDS micelle. With increasing surfactant concentration, the change in the extinction coefficients decreased in the order  $R-1 > R-2 > R-3$  for both the

Fig. 6. Dependence of the extinction coefficients on surfactant concentration for three acid dyes in the absence and presence of PVP at  $25^\circ\text{C}$  (R-1;  $492 \text{ nm}$ , R-2;  $494 \text{ nm}$ , R-3;  $509 \text{ nm}$ ).





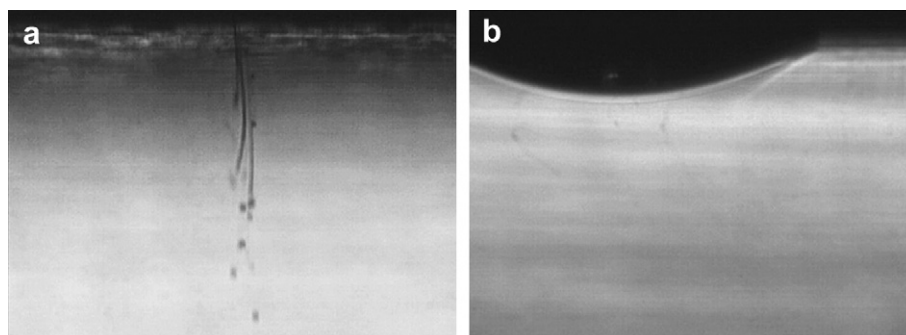
**Scheme 1.** Models for the ternary systems (R-1/PVP/SDS and R-1/PVP/S465) in aqueous solutions.



**Fig. 8.** Change of the viscosity and the surface tension of the ink solutions as a function of S465 concentration at 25 °C.

surfactants. This means that increasing solubility of the dyes (the increasing number of sulfonate groups) decreases the binding affinity of the dyes to the surfactant micelles.

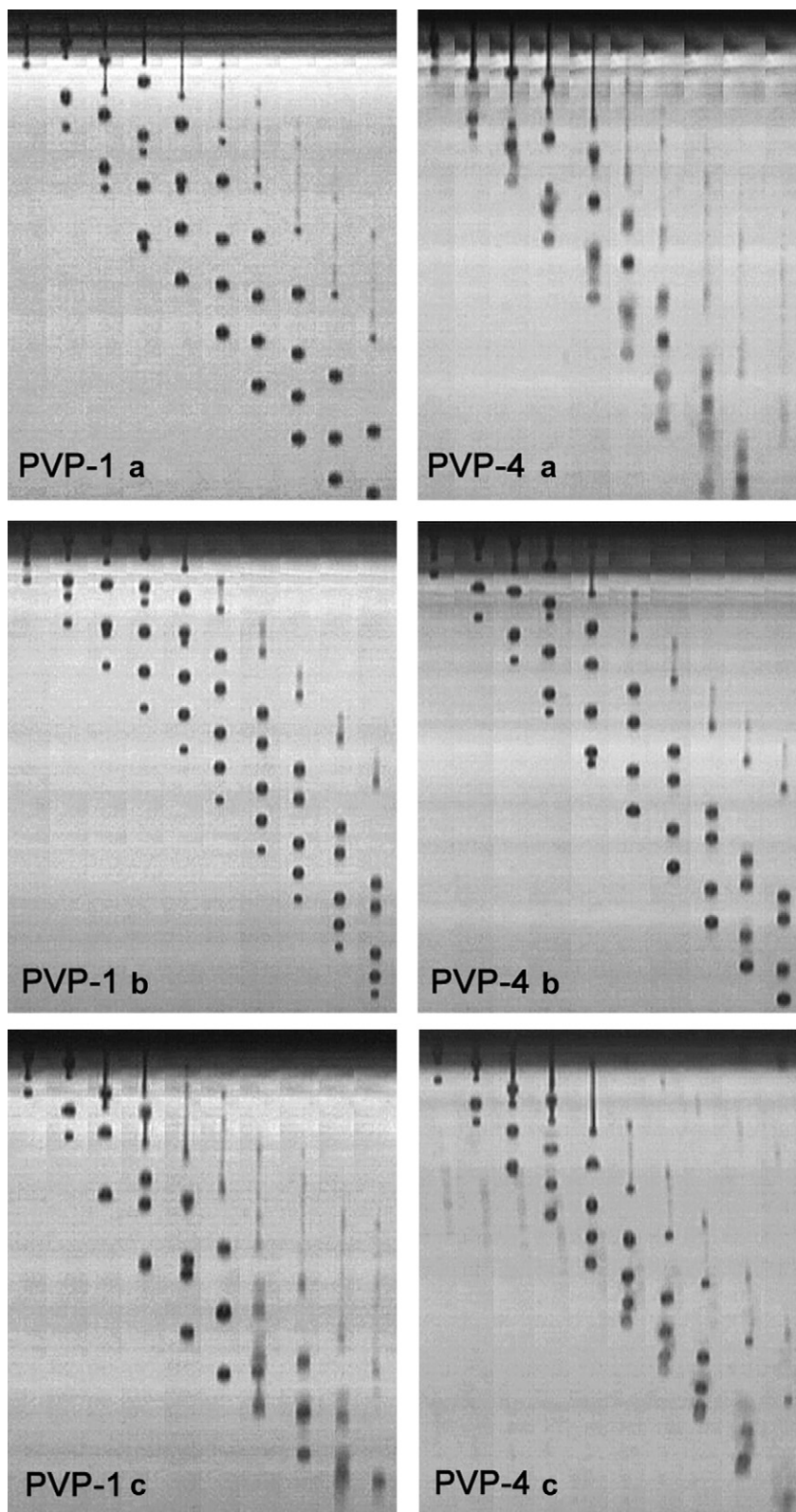
For SDS, the extinction coefficients decreased with the addition of PVP alone (see the ordinate axis in Fig. 6) and increased with further addition of SDS. The magnitude of the change was different for different dyes. This suggests that the binding of the dye molecules with PVP is broken by the addition of SDS: the SDS micelles remove the dyes from PVP. A similar tendency has been observed for the efficacy of SDS in an azo dye/poly(vinylpyridine-*n*-oxide) system [42]. This can be attributed to the dyes and SDS having negatively charged groups while PVP has a partial positive charge, so there is an electrostatic attraction between PVP and the dyes or SDS. Increasing the SDS concentration will replace the dye anions with SDS anions. This replacement becomes easier in the order R-1 < R-2 < R-3. For S465, the change in the extinction coefficients decreased in the order R-1 > R-2 > R-3 with increasing S465 concentration in the presence of PVP. This is because the binding capability of the dyes with S465 decreases in the order R-1 > R-2 > R-3 [46] (the binding constants of dyes with S465: R-1, 7200 dm<sup>3</sup> mol<sup>-1</sup>; R-2, 4880 dm<sup>3</sup> mol<sup>-1</sup>; and R-3, 2100 dm<sup>3</sup> mol<sup>-1</sup>). Fig. 7 shows the extinction coefficients of the S465 concentration for R-1 in the absence and presence of the three types of PVPs at 25 °C. The addition of only PVP decreases the



**Fig. 9.** Fluids emerging from a DOD print head. (a) PVP-1/S465 (1.4/0.002 mol dm<sup>-3</sup>) (b) PVP-63/S465 (0.135/0.003 mol dm<sup>-3</sup>).

extinction coefficients, while further addition of S465 increases them for all the PVPs. No effect of polymer molecular weight was observed. From the above results, the model for the dye/additive interaction is shown in [Scheme 1](#).

Thus, the anionic surfactant influences the dye behavior in the three-species system, whereas the nonionic surfactants have little effect. In other words, the type of head groups in the surfactants plays an important role for the three-species systems.



**Fig. 10.** Generation patterns of inkjet drops of different ink compositions. PVP-1; 1.4 mol dm<sup>-3</sup>/S465 (a) 0.003, (b) 0.004, (c) 0.005 mol dm<sup>-3</sup>. PVP-4; 0.7 mol dm<sup>-3</sup>/S465 (a) 0.003, (b) 0.004, (c) 0.005 mol dm<sup>-3</sup>.

### 3.2. Physicochemical properties and droplet formation of ink solution

#### 3.2.1. Viscosity and surface tension

The change of the viscosity in the ink solutions with S465 concentration at 25 °C is shown in Fig. 8. To obtain adequate viscosity of the ink solutions, the concentrations of PVP used were 1.4, 0.7, and 0.135 mol dm<sup>-3</sup> for PVP-1, PVP-4, and PVP-63, respectively. The different polymer concentrations are because of different molecular weights of the PVPs. A similar tendency was observed in a previous study [55], in which the viscosity of aqueous PVP solutions increased with increasing molecular weight. The viscosity values of PVP-1, PVP-4 and PVP-63 in the absence of S465 were 3.33, 3.34 and 3.33 mPa s, respectively. The addition of S465 to the ink slightly increased the viscosity in the concentration range considered. This is due to an increase in the strength of the hydrophobic chain interaction, owing to the adsorption of individual surfactant molecules [56].

The surface tension values are plotted in Fig. 8 as a function of surfactant concentration. The surface tension greatly decreased by the addition of S465, but it was almost unaffected by the polymer molecular weight.

#### 3.2.2. Droplet formation

Fig. 9 shows the ejection images of the ink solutions with a discharge voltage of 22 V. The ejection images of the R-1/PVP-1/S465 ink with adequate viscosity but inadequate surface tension are shown in the Fig. 9a. This image shows the unstable ink drops from some nozzles with mist generation. This indicates that it is necessary to adjust not only the viscosity but also the surface tension for stable ink droplet formation. Similar images were observed for PVP-4 in the same S465 concentration range. In the case of PVP-63 (Fig. 9b), no discharge was observed. The ink only leaks out of the nozzle, and the inkjet discharge property is very poor. For all the inks containing different concentrations of PVP-63 and S465, similar results to the image shown in Fig. 9b were observed. This suggests that PVP-63, which has a high molecular weight, can easily cause clogging problems due to entanglement and fluidity decline.

On the other hand, for PVP-1 and PVP-4 the compositions of the ink solutions having adequate viscosity (3–4 mPa s) and surface tension (33–36 mN m<sup>-1</sup>) are shown in the area of deviant crease lines in Fig. 8. The ink drops were formed with a discharge voltage of 22 V and a discharge drop number of 5 (Fig. 10). Each image shows the first five drops of ink ejected for different compositions.

In the case of the PVP-1 (b), 5 spherical drops were observed, while PVP-1 (a) and PVP-4 (b) showed 4 spherical drops. This suggests that the existence of a long tail of drops creates the satellite drops, and the satellite drops collide with each other or with the main drops, because of an excess of velocity of the main drops. In the case of PVP-1 (c), PVP-4 (a), and PVP-4 (c), spherical drops were not formed, with the ink instead forming very long and broken tails. PVP-1 (Fig. 10b) (PVP-1/S465 = 1.4/0.004 mol dm<sup>-3</sup>) ink solution resulting in excellent ink droplet formation had a shorter tail length, a longer breakup time, a smaller drop size and stable drop ejection. Therefore, addition of PVPs with low molecular weights results in better ink droplets. A similar tendency has been observed in previous studies [57,58]. It was found that the following average molecular weight ranges of PVP are adequate for the good droplet formation: preferably from 2000 to 30,000, and ideally from 5000 to 15,000 [57]; preferably from 3000 to 100,000, more preferably from 4000 to 50,000, and ideally from 1500 to 40,000 [58].

#### 3.2.3. Visible absorption spectra

The visible absorption spectral change was investigated to elucidate the dye/additive interactions in inkjet ink solutions as shown in Fig. 11. In the case of R-1/S465/PVP-1, the color of the ink solutions changed to light yellow due to high polymer concentration. The addition of PVP-4 increased the maximum absorption wavelength (red shift) and the extinction coefficient decreased. This indicates that the dye molecules strongly bind to the PVP chain in the concentration range of ink solutions considered. A similar change was observed for PVP-63.

To analyze the spectral change with S465 concentration, the extinction coefficients at the wavelength where the largest difference was observed were used. As shown in Fig. 12, the extinction coefficients at 488 nm decreased with the addition of all the PVPs, but the extinction coefficients did not significantly change with increasing S465 concentration. However, the change of the extinction coefficients differs from the results shown in Fig. 6, due to the lower concentration range of S465 (below cmc) and higher PVP concentrations. This indicates that the dye molecules strongly bind to the PVP chain for all the PVP molecular weights in the concentration range of ink solutions considered.

From the above results, the best ink droplet formation was observed for an ink composition with adequate physicochemical properties that contained PVP with low molecular weight, although the color of the ink changed to light yellow due to the high concentration of PVP-1. Furthermore, in the optimized ink composition the dye molecules were strongly bound to the PVP

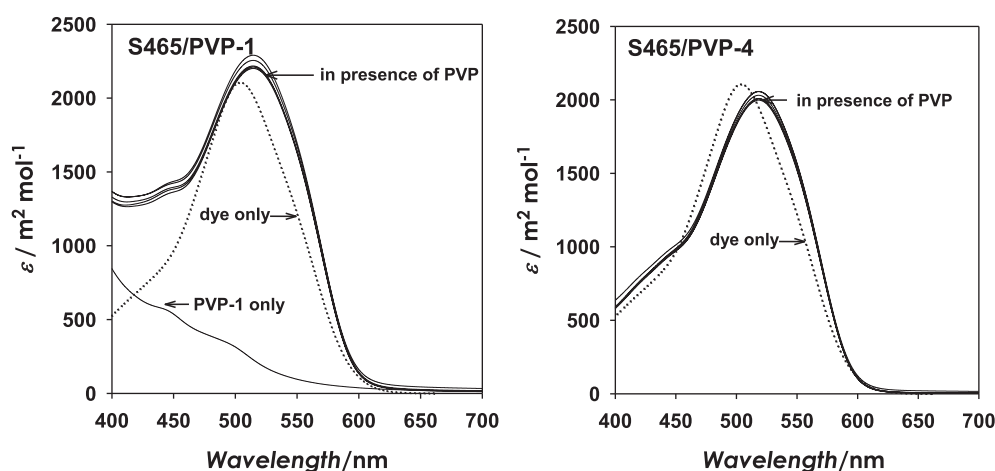


Fig. 11. Visible absorption spectra of R-1 ink solutions with S465 concentration in the absence and presence of PVP at 25 °C (PVP-1; 1.4, PVP-4; 0.7 mol dm<sup>-3</sup>).



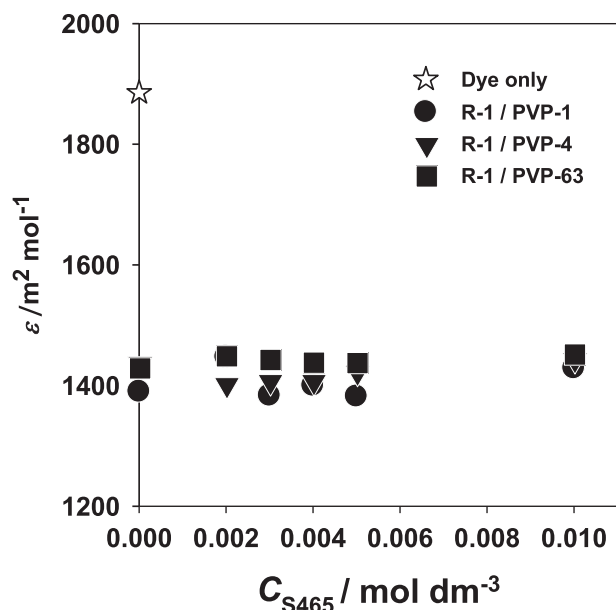


Fig. 12. Dependence of the extinction coefficients on S465 concentration for R-1 in the absence and presence of the PVP at 25 °C and 488 nm (PVP-1; 1.4, PVP-4; 0.7, PVP-63; 0.135 mol dm<sup>-3</sup>).

chains, while binding was not significantly affected by the addition of S465.

#### 4. Conclusions

The visible absorption spectral change of aqueous dye solutions with constant concentrations of the dyes and surfactants and various polymer concentrations was different for nonionic and anionic surfactants. In the case of nonionic surfactants, the spectra changed with the addition of the surfactants but were unchanged by further addition of PVP, indicating that the strong binding of dye molecules with the nonionic surfactant micelles is maintained even in the presence of PVP. In contrast, in the case of the anionic surfactant the spectra changed with the addition of the surfactant as well as with further addition of PVP.

In addition, the influence of surfactant concentrations in the aqueous solutions including the dyes and PVP with constant concentrations was investigated. The addition of PVP decreased the extinction coefficient at the maximum absorption wavelength, and it then increased with increasing surfactant concentrations. This suggests that the surfactants hinder the binding of the dye to PVP, leading to the incorporation of the dye into the surfactant micelles. Furthermore, the spectral change with increasing surfactant concentrations for anionic surfactants was greater than for nonionic surfactants.

From the results of ink droplet formation, for all the ink solutions containing PVP-63 and S465 the ejection property was very poor, even though the inks have adequate viscosity and surface tension. The composition of the ink solutions resulting in excellent ink droplet formation had appropriate physicochemical properties such as viscosity and surface tension as well as a PVP with low molecular weight. In the optimized ink composition (PVP-1/S465: 1.4/0.004 mol dm<sup>-3</sup>), most of the dye molecules are strongly bound to the PVP chain and the binding was hardly affected by the addition of S465.

One of the purposes in this study is the elucidation of the relationship between the dye/additive interaction and ink droplet formation in order to obtain a measure to select adequate dyes and additives in the ink. However, no clear-cut relationship between

the binding behavior and the droplet formation was found. In the future, binding behavior should be investigated energetically to help guide the selection of dyes and additives. Furthermore, the studies on more detailed ink performance are required the effects of temperature on interactions within the fluids and droplet properties of ink solutions as well as the performance of the printed fabrics printability, to the creation of a meaningful ink composition and development of ink performance.

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