

Relationship between the Dye/Additive Interaction and the Inkjet Ink Performance

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ABSTRACT

To design adequate ink composition for textile printing, the relationship between the dye/additive interaction and the ink performance are investigated. In the present study, 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 hardly changed, 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 further addition of PVP. From the above results, the behavior of the acid dyes in three species coexistence system depends on the dye structure, the surfactant structure, the molecular weight of PVP, and so on. Furthermore, to estimate the ink performance, the physical properties of the ink such as viscosity, surface tension, and ink droplet formation were determined. The composition of the ink solution having excellent ink droplet

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formation was observed, which had appropriate physicochemical properties such as viscosity and surface tension as well as PVP with lower molecular weight. 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 was hardly affected by the addition of S465.

Keywords: acid dye; additive; interaction; inkjet ink; droplet formation

1. Introduction

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

In the inkjet ink, various interactions such as dye-dye, dye-additive and additive-additive interactions are observed. There are a lot of studies on the dye aggregation [14-21], dye/polymer interaction [22-28], dye/surfactant interaction [29-34], polymer/surfactant interaction [35-39], and dye/polymer/surfactant interaction [40-43]. However, there is no fundamental study on the relationship between the dye/additive interaction and the ink performance.

In our previous study [44], the dye-dye interaction, *i.e.* the aggregation behavior of three acid dyes (C. I. Acid Red 88, 13, and 27) containing different number of sulfonate groups was investigated. As a result, the higher was the solubility of the dyes in water, the lower were the aggregation constants of the dyes. Also, the dye-additive interaction, *i.e.* the interaction of the acid dyes with a water-soluble polymer additive,

poly(vinylpyrrolidone) (PVP) and surfactant micelles were investigated [45,46]. 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 to PVP and the surfactant micelles, indicating that the hydrophobic interaction is strongly concerned with the binding processes. Furthermore, the binding constants of the dyes with PVP were diminished by increasing molecular weight of PVP [45]. The binding constants for the nonionic surfactants, octaethylene glycol monododecyl ether (OGDE) and Surfynol 465 (S465), were much larger than those for the anionic surfactant, sodium dodecyl sulfate (SDS), suggesting that the electrostatic repulsion between the negatively charged groups of the dyes and SDS diminishes the affinity [46]. From the above results, it is concluded that the binding affinities were influenced by the dye structure, the polymer molecular weight, the surfactant structure, the micelle shape, and so on.

On the other hand, the physicochemical properties of ink for textile printing should be optimized for specified inkjet technology, print heads and various printing devices [1,4,11,47-49]. The main parameters which 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]. The 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 the surface tension of the ink [1,12]. For adequate droplet formation, the viscosity of the ink should be kept low to get good jetting properties [52], and the surface tension must be such that the ink wets the capillary channels and flows through the nozzle [1]. Although the physical properties are dependent on the print head and ejection conditions, typical inkjet ink should have the

surface tension of 25 - 50 mN m⁻¹, and the viscosity of 1 - 25 mPa s [53]. Thus, in order to prepare the ink having adequate viscosity and surface tension, polymers are used to control the viscosity and surfactants are added to control the surface tension [53].

In the present 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 including both a water-soluble polymer, (poly(vinylpyrrolidone) (PVP)) and the surfactants (sodium dodecyl sulfate (SDS), octaethylene glycol monododecyl ether (OGDE), and Surfynol 465 (S465)) is investigated by means of visible absorption measurements. The effects of PVP concentration in the aqueous solutions including the dyes and the surfactants with constant concentrations as well as the influences of the surfactant concentration in the aqueous solutions including the dyes and PVP with constant concentrations were investigated. Furthermore, to estimate the ink performance, the physical properties of the ink such as viscosity, surface tension, and ink droplet formation were determined. From these results, the relationship between the dye/additive interaction and the ink performance is discussed.

2. Experimental

2.1 Materials

Three acid dyes containing the different number 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 commercially purchased from Tokyo Chemical Industry Co., Ltd., and used after purification, and R-2 was prepared by coupling diazotized 4-amino-1-naphthalenesulfonic acid with sodium 2-hydroxy-6-naphthalenesulfonate under alkaline conditions and purified as described in a previous paper [44].

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

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

(Fig.1)

2.2 Methods

2.2.1 Visible absorption spectroscopy

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

2.2.2 Ink preparation

From the viewpoint of discharge property of inkjet head, the viscosity of 3 - 4 mPa s and the surface tension of 33 - 36 mN m⁻¹ at 25 °C are desirable in the present study. To adjust the adequate viscosity, the concentrations of the polymers were set up as 1.4, 0.7, 0.135 mol dm⁻³ for PVP-1, PVP-4, PVP-63, respectively. To adjust the adequate surface tension, the surfactant (S465) concentrations were set up in the range of 0 – 0.01 mol dm⁻³. The dye concentration of 2.97×10^{-5} mol dm⁻³ was remained.

2.2.3 Viscosity and surface tension measurements.

The viscosity of the ink solutions was measured by using 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 ink at 25 °C.

2.2.4 Droplet formation measurements

The formation of ink droplet was measured by JetLyzer (Mimaki Engineering Co., Ltd. Ver. T-0.782) equipped with a CA4 inkjet print head (Toshiba Tec Corporation). The droplet firing condition was 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 including both PVP and the surfactants

3.1.1 Influence of PVP concentration in the aqueous solutions including the dye and the surfactants with constant concentrations

The visible absorption spectral change of aqueous R-1 solutions with PVP-1 concentration in the presence of the surfactants is represented in Fig. 2. The maximum absorption wavelength shifted to higher wavelength (red shift) with the addition of the surfactants. In the case of the nonionic surfactant, OGDE, its addition changed the spectra, but further addition of PVP hardly changed. The similar spectral change was observed for the nonionic gemini surfactant, S465. In contrast, in the case of the anionic surfactant, SDS, the spectra were changed by the addition of the surfactant as well as further addition of PVP.

(Fig.2)

To analyze the spectral change with PVP concentration, the extinction coefficients, ϵ , at the wavelength where the largest difference was observed (492 nm) are useful. 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 hardly changed 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, in the case of SDS, the extinction coefficients decreased with increasing PVP concentration, indicating that the dyes are bound with PVP. This result might be due to the fact that PVP influences the behavior of SDS micelles and the dye is easier to bind with PVP rather than SDS micelles.

(Fig.3)

In our previous study [46], particularly in the case of OGDE, the binding affinity of the dyes with the micelles was heavily dependent on the solubility of the acid dyes in water (the binding constants of the dyes with OGDE micelles: R-1, not determined but

much more than R-2; R-2, $260000 \text{ dm}^3 \text{ mol}^{-1}$; R-3, $3200 \text{ dm}^3 \text{ mol}^{-1}$). To discuss the effects of the dye structure in aqueous solutions including three species in more detail, the change of the extinction coefficients with PVP-1 concentration were investigated for three acid dyes having the different number of the sulfonate groups (Fig. 4). In the absence of PVP (see the ordinate axis in Fig. 4), the extinction coefficients were diminished by the addition of OGDE. The degree of the decrease was the order of R-3 < R-2 < R-1, which corresponds to the increasing order in the affinity of the dyes with the surfactant micelles (R-3 < R-2 < R-1) determined in the previous study [46]. Furthermore, the manner in the change of the extinction coefficients with PVP concentration was quite different among three dyes. In the case of R-1/OGDE, the extinction coefficients hardly changed with increasing PVP concentration. This suggests that all R-1 molecules are incorporated into the OGDE micelles and 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 dyes may be bound to the PVP chains. In the case of aqueous R-3 solutions, the presence of OGDE did not influence the dependence of the extinction coefficients with increasing PVP concentration. This suggests that all R-3 molecules are never incorporated into the OGDE micelles owing to their high water solubility. Thus, in the R-2/OGDE and R-3/OGDE solutions, the anionic groups of the remaining free dyes are believed to interact with the positively charged pyrrolidone rings (pyrrolidone carries partially positive charge on the nitrogen atom) as was pointed out in the previous study [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 is the affinity with the surfactant micelles, the lower is the binding force with PVP.

(Fig.4)

3.1.2 Influence of the surfactant concentration in the aqueous solutions including the dyes and PVP with constant concentrations

Fig. 5 shows the influence of the surfactant concentrations upon 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 higher wavelength (red shift) and the extinction coefficient at that wavelength was decreased by the addition of PVP alone. Further addition of the surfactants increased the extinction coefficients. The similar spectral change was also observed for R-2 and R-3. This suggests that the surfactants hinder the binding of the dye with PVP, leading to the incorporation of the dyes into the surfactant micelles. Furthermore, the spectral change with increasing surfactant concentration for aqueous R-1/PVP/SDS solutions was bigger than that for aqueous R-1/PVP/S465 solutions, because PVP might be bound to SDS rather than S465. This result is in agreement with the tendency described in a literature [37], in which the association of an ionic surfactant to a hydrophilic homopolymer is strongly cooperative, whereas a nonionic surfactant shows weak interaction with most homopolymers. The addition of SDS brings unfolding of the PVP chains [54] and SDS should interact more easily with the positively charged pyrrolidone rings of PVP (pyrrolidone carries partially positive charge on the nitrogen atom).

(Fig.5)

The relative efficacy of the surfactant concentrations on the extinction coefficients in the aqueous solutions including the dyes and PVP is shown in Fig. 6. In the absence of PVP, the degree of change in the extinction coefficients for the aqueous S465 solutions was bigger than that for the aqueous SDS solutions, indicating that the acid dyes should be bound to the S465 micelle rather than the SDS micelle. With increasing surfactant concentration, the degree of the change in the extinction coefficients decreased in the

order of $R-1 > R-2 > R-3$ for both the surfactants. This means that the increasing solubility of the dyes (the increasing number of sulfonate groups) decreases the binding affinity of the dyes with the surfactant micelles.

(Fig.6)

In the case of SDS, the extinction coefficients were decreased by the addition of PVP alone (see the ordinate axis in Fig. 6) and further addition of SDS increased them. The manner of the change varied from dye to dye. This suggests that the binding of the dye molecules with PVP should be broken by the addition of SDS: the SDS micelles should grab the dyes from PVP. The similar tendency was observed for the efficacy of SDS in an azo dye/poly(vinylpyridine-*n*-oxide) system [42]. This result might be explained as follows. The dyes and SDS have negatively charged groups. PVP has partially positive charge, so that the electrostatic interaction acts between PVP and the dyes or SDS. The increase of SDS concentration should replace the dye anions with SDS anions. This replacement becomes easier in the order of $R-1 < R-2 < R-3$. On the other hand, in the case of S465, the degree of the change in the extinction coefficients decreased in the order of $R-1 > R-2 > R-3$ with increasing S465 concentrations in the presence of PVP. This is because the binding capability of the dyes with S465 decreased in the order of $R-1 > R-2 > R-3$ as already described in previous study [46] (the binding constants of dyes with S465: R-1; 72000, R-2; 4880, R-3; $2100 \text{ dm}^3 \text{ mol}^{-1}$). Fig. 7 shows the extinction coefficients on S465 concentration for R-1 in the absence and presence of three kinds of PVP's with different molecular weights at 25 °C. The addition of PVP alone decreased the extinction coefficients and further addition of S465 increased them for all the PVP's. In this behavior, any effects of polymer molecular weight were not observed. From the above results, the model for the dye/additive interaction might be depicted in Scheme 1.

(Fig.7)

(Scheme 1)

Thus the anionic surfactant greatly influences the dye behavior in three species coexistence system, whereas the nonionic surfactants hardly affects. In other words, the kinds of the head groups in the surfactants play an important role under the coexistence of three species.

3.2 Inkjet ink performance

3.2.1. Viscosity and surface tension

The change of the viscosity in the ink solutions with S465 concentration at 25 °C is given in Fig. 8. To obtain the adequate viscosity value, the concentrations of PVP were set up as 1.4, 0.7, 0.135 mol dm⁻³ for PVP-1, PVP-4, PVP-63, respectively. These different polymer concentrations are caused by the distinction of the molecular weight. The similar tendency was observed in a literature [55], in which the viscosity of aqueous PVP solutions regularly 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 into the ink slightly increased the viscosity values in the concentration range under examination. This is due to an increase in the strength of the hydrophobic chain interaction resulting from the adsorption of individual surfactant molecules [56].

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

(Fig.8)

3.2.2. Visible absorption spectra

The visible absorption spectral change of the prepared inkjet ink solutions is shown in Fig. 9. In the case of R-1/S465/PVP-1, the color of the ink solutions changed to light

yellow due to high polymer concentrations. The addition of PVP-4 made the maximum absorption wavelength to be higher (red shift), and the extinction coefficient to be smaller. This is due to the fact that the anionic groups of the dyes interact with the positively charged pyrrolidone rings. The similar spectral change was observed for PVP-63.

(Fig.9)

To analyze the spectral change with S465 concentration, the extinction coefficients, ϵ , at the wavelength where the larger difference was observed are useful. As shown in Fig. 10, the extinction coefficients at 488 nm were decreased by the addition of all PVP's, but the extinction coefficients hardly changed with increasing S465 concentration. On the other hand, the change of the extinction coefficients was differed from the result shown in Fig. 6, due to the lower concentration range of S465 (below cmc) and higher PVP concentrations. Thus, this indicates that the dye molecules strongly bind to the PVP chain in concentration range of ink solutions, for all the PVP molecular weights.

(Fig.10)

3.2.3. Droplet formation

Fig. 11 shows the ejection images of the ink solutions at the discharge voltage of 22 V. The ejection images of the R-1/PVP-1/S465 ink having adequate viscosity and inadequate surface tension are presented in the Fig. 11a, b, and c. These images show the only mist generation (a) and unstable ink drops from some nozzle with mist generation (b and c). This indicates that it is necessary to adjust not only the viscosity but also the surface tension for the stable ink droplet formation. The similar images were observed for PVP-4 in the same S465 concentration ranges. In the case of PVP-63 (Fig. 11d), no discharge was observed, in which only the ink leaks out of the nozzle, and the inkjet discharge property was very poor. For all the ink containing PVP-63

and S465 with different concentrations, similar results to the image shown in Fig. 11d were observed. This suggests that PVP-63 with higher molecular weight can easily cause clogging problems due to the entanglements and the fluidity decline.

On the other hand, in the case of PVP-1 and PVP-4, the compositions of the ink solutions having the adequate viscosity (3 - 4 mPa s) and the appropriate surface tension (33 - 36 mN m⁻¹) are shown in the area of deviant crease lines in Fig. 8. The ink drops were formed at the discharge voltage of 22 V and the discharge drop number of 5, as shown in the Fig. 12. Each image shows the first five drops ejected in the ink with 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 long tail of drops creates the satellite drops, and the satellite drops cause to collide with each other or with the main drops because of an excess of the velocity of the main drops. In the case of PVP-1(c), PVP-4(a), and PVP-4(c), the spherical drops were not formed, and very long and broken tails were formed. In the case of PVP-1(b) (PVP-1/S465 = 1.4/0.004 mol dm⁻³), the excellent ink droplet formation was observed, although the color of the ink changed to light yellow due to the high concentration of PVP-1, as was described previously. Accordingly, PVP having the lower molecular weight makes it possible to form a better droplet of the inkjet ink. The similar tendency was also observed in previous studies [57,58]. It is found that the following weight average molecular weight range of PVP is adequate for the better droplet formation: preferably from 2,000 to 30,000, and more preferably from 5,000 to 15,000 [57], preferably from 3,000 to 100,000, more preferably from 4,000 to 50,000, and further preferably from 1,500 to 40,000 [58].

(Fig.11)

(Fig.12)

From the above results, the excellent ink droplet formation was observed for an ink

composition, which had an appropriate physicochemical property and included PVP with lower molecular weight. Especially, the molecular weight of PVP played an important role in the ink droplet formation. Furthermore, in this optimized ink composition, the dye molecules were strongly bound to the PVP chains, but the binding was hardly affected by the addition of S465.

4. Conclusions

The visible absorption spectral change of aqueous dye solutions including the constant concentrations of the dyes and the surfactants with polymer concentration was different between the nonionic and anionic surfactant. In the case of the nonionic surfactants, the spectra changed with the addition of the surfactants, but further addition of PVP hardly changed, 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 further addition of PVP.

Also, 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 then increased with increasing surfactant concentrations. This suggests that the surfactants hinder the binding of the dye with PVP, leading to the incorporation of the dye into the surfactant micelles. And the spectral change with increasing surfactant concentrations for anionic surfactant was bigger than that for nonionic surfactants.

From the results of the ink performance, for all the ink solutions containing PVP-63 and S465, the ejection property was very poor, although they have adequate viscosity and surface tension. The composition of the ink solution having excellent ink droplet formation was observed, which had appropriate physicochemical properties such as

viscosity and surface tension as well as PVP with lower molecular weight. 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 was hardly affected by the addition of S465.

Thus, the elucidation of the relationship between the dye/additive interaction and the ink performance should contribute to the improvement of inkjet ink for textile printing.

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ink composition, ink set, and image forming method. United States patent US
20110025753, 2011 Feb 3.

SEQUENCE OF FIGURES AND SCHEME THAT APPEARED IN THE MANUSCRIPT

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

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).

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 mol dm⁻³).

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

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

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

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 mol dm⁻³) with different molecular weights at 25 °C and 492 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.

Fig. 9 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⁻³).

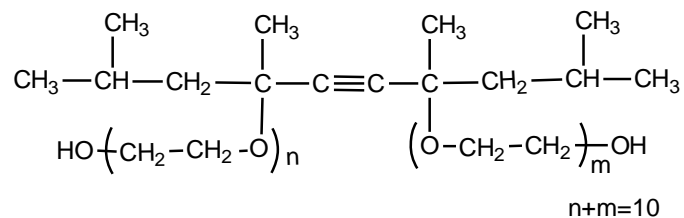
Fig. 10 Dependence of the extinction coefficients on S465 concentration for R-1 in the absence and presence of the PVP at 25 °C and 488 nm (PVP-1; 1.4, PVP-4; 0.7, PVP-63; 0.135 mol dm⁻³).

Fig. 11 Fluids emerging from a DOD print head.

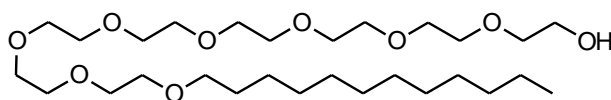
(a) PVP-1/S465 (1.4/0 mol dm⁻³), (b) PVP-1/S465 (1.4/0.002 mol dm⁻³),
(c) PVP-1/S465 (1.4/0.01 mol dm⁻³), (d) PVP-63/S465 (0.135/0.003 mol dm⁻³)

Fig. 12 Generation patterns of inkjet drops of different ink compositions.

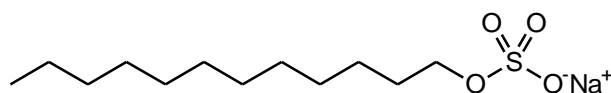
PVP-1; 1.4 mol dm⁻³ / S465 (a) 0.003, (b) 0.004, (c) 0.005 mol dm⁻³
PVP-4; 0.7 mol dm⁻³ / S465 (a) 0.003, (b) 0.004, (c) 0.005 mol dm⁻³



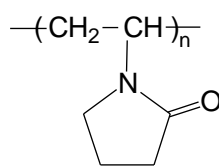
S465



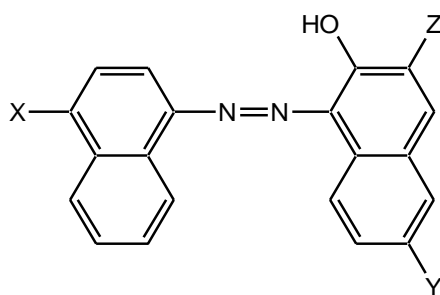
OGDE



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.

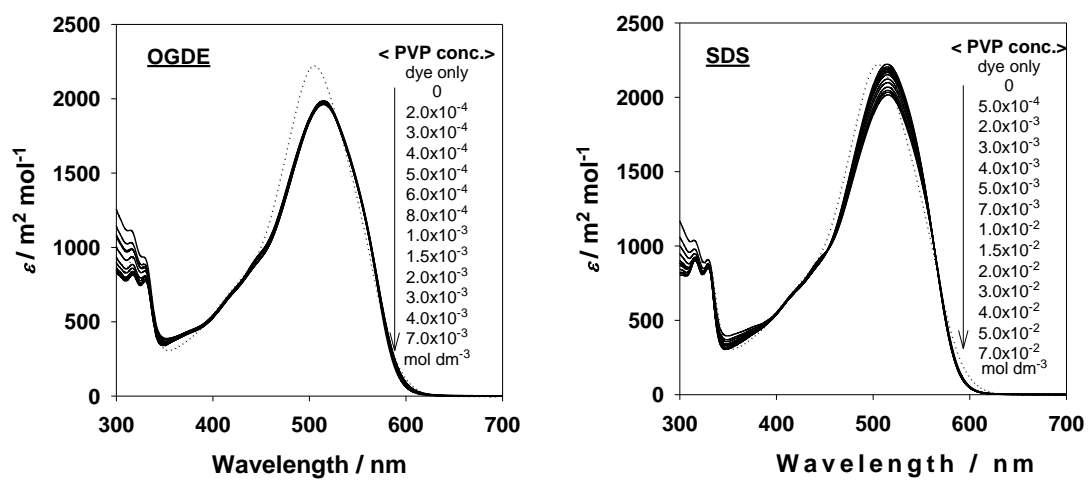


Fig. 2 Visible absorption spectral change of aqueous R-1 solutions with PVP-1 concentration in presence of the surfactants at 25 °C (OGDE; 0.006, SDS; 0.05 mol dm⁻³).

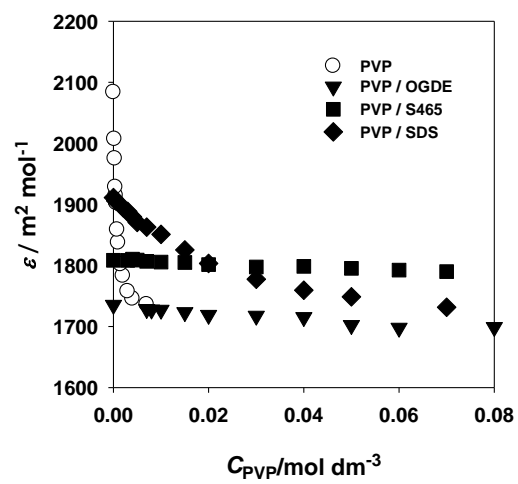


Fig. 3 Dependence of the extinction coefficients on PVP-1 concentration for R-1 in the absence and presence of the surfactants at 25 °C and 492 nm (OGDE; 0.006, S465; 0.02, SDS; 0.05 mol dm⁻³).

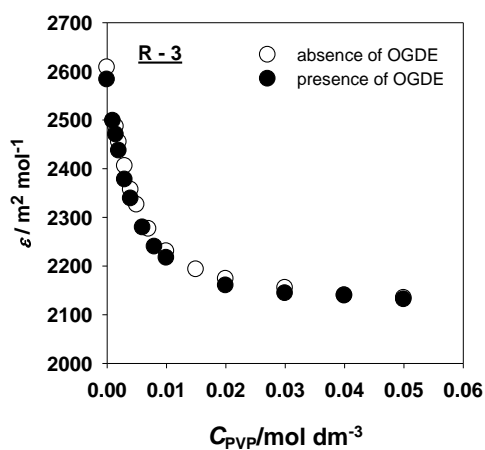
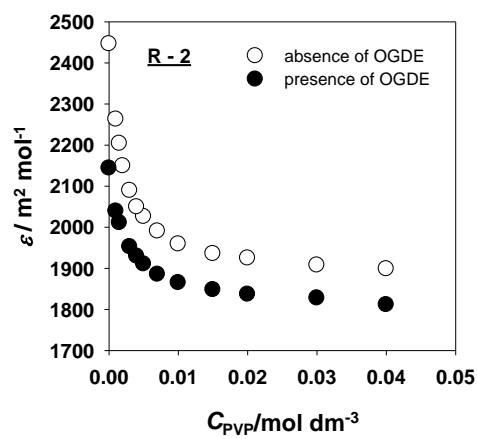
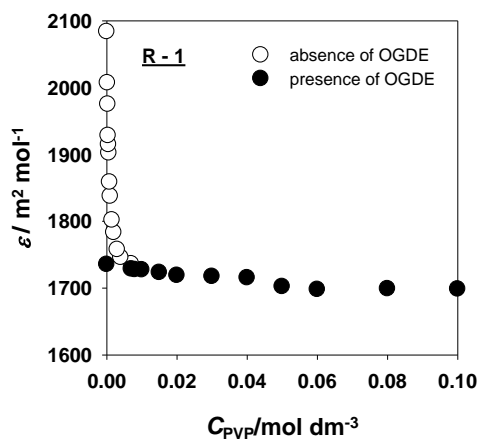


Fig. 4 Dependence of the extinction coefficients on PVP-1 concentration for three acid dyes in the absence and presence of OGDE ($0.006 \text{ mol dm}^{-3}$) at $25 \text{ }^\circ\text{C}$ and 492 nm .

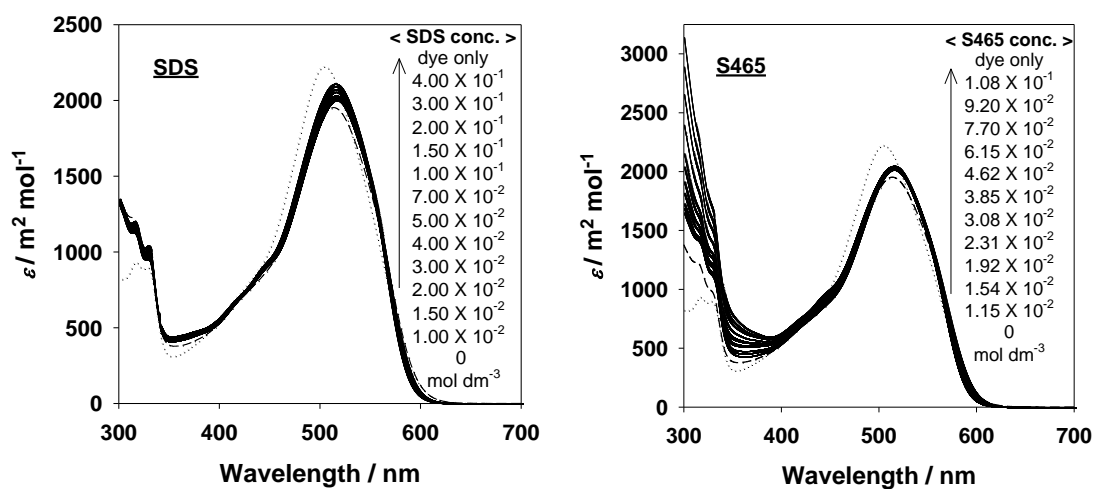


Fig. 5 Visible absorption spectra change of aqueous R-1 solutions with SDS and S465 concentration in presence of PVP (0.1 mol dm^{-3}) at $25 \text{ }^\circ\text{C}$.

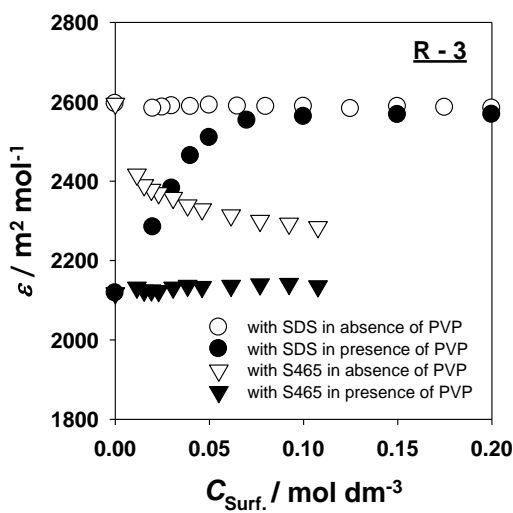
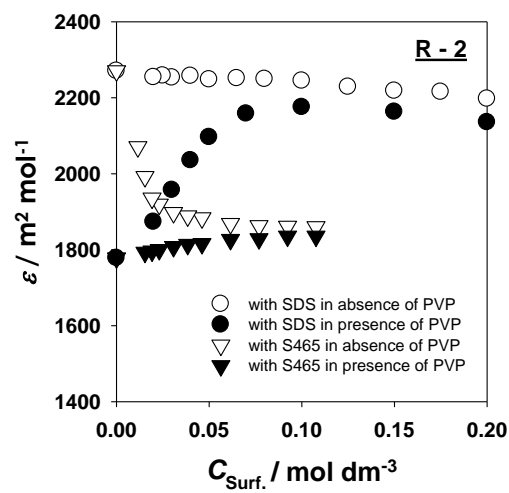
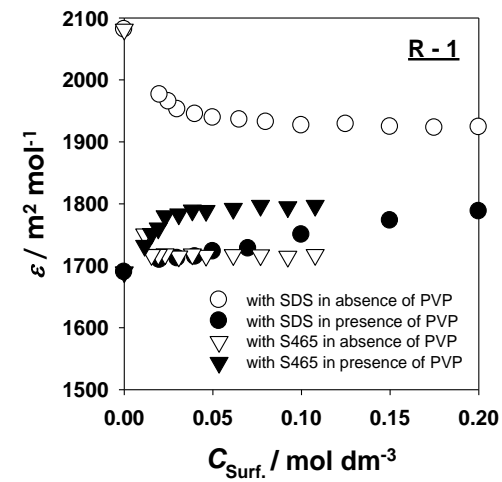


Fig. 6 Dependence of the extinction coefficients on surfactant concentration for three acid dyes in the absence and presence of PVP at 25 °C (R-1; 492 nm, R-2; 494 nm, R-3; 509 nm).

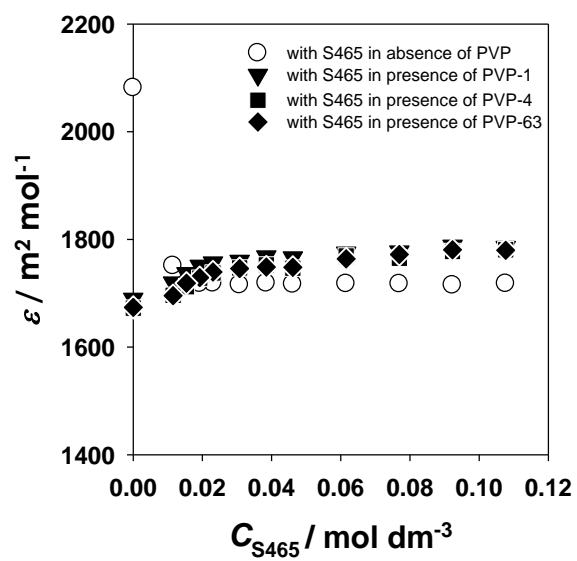
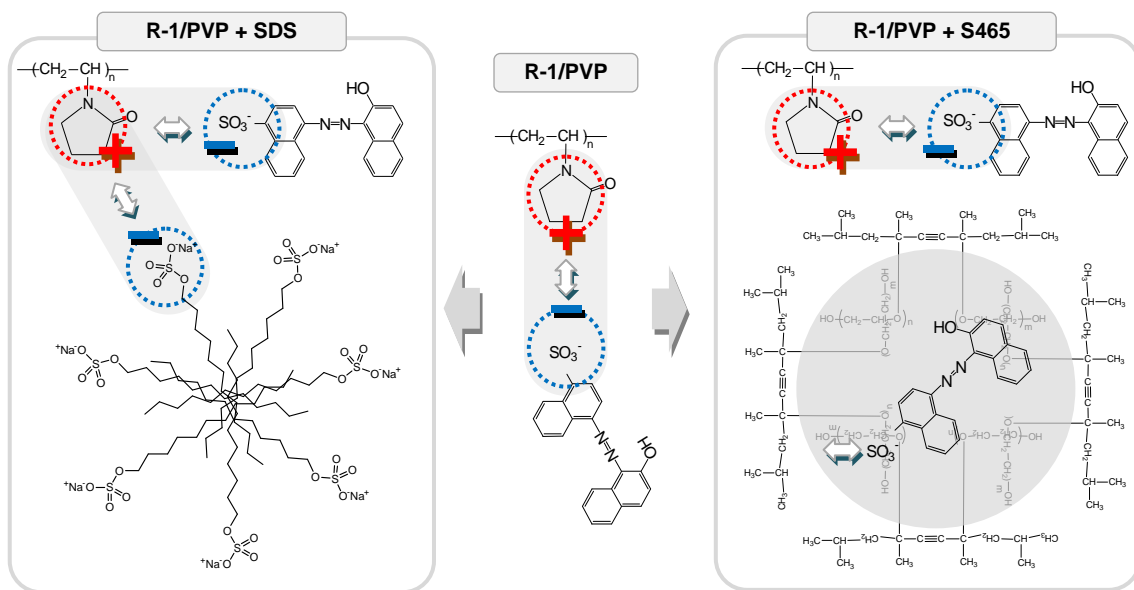


Fig. 7 Dependence of the extinction coefficients on S465 concentration for R-1 in the absence and presence of three kinds of PVP's (0.1 mol dm^{-3}) with different molecular weights at $25 \text{ }^\circ\text{C}$ and 492 nm .



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

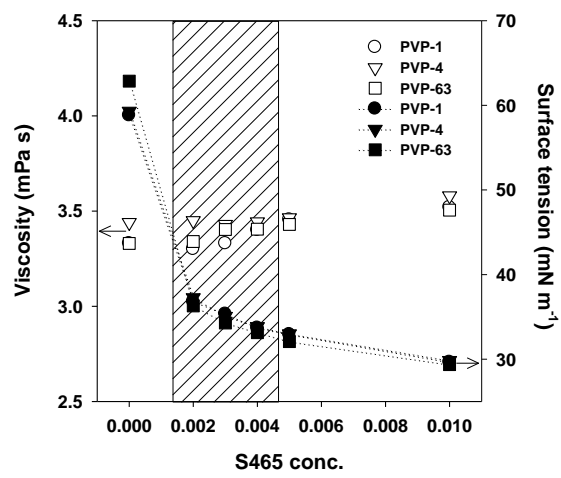


Fig. 8 Change of the viscosity and the surface tension of the ink solutions as a function of S465 concentration at 25 °C.

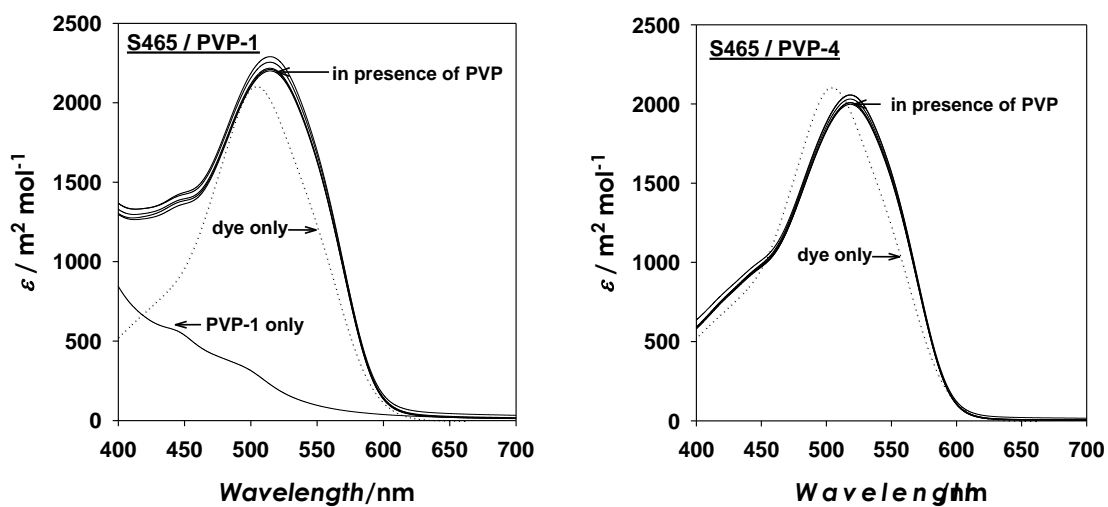


Fig. 9 Visible absorption spectra of R-1 ink solutions with S465 concentration in the absence and presence of PVP at 25 °C (PVP-1; 1.4, PVP-4; 0.7 mol dm⁻³).

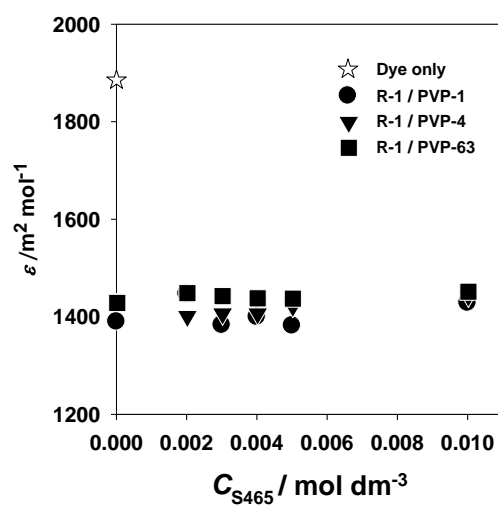


Fig. 10 Dependence of the extinction coefficients on S465 concentration for R-1 in the absence and presence of the PVP at 25 °C and 488 nm (PVP-1; 1.4, PVP-4; 0.7, PVP-63; 0.135 mol dm⁻³).

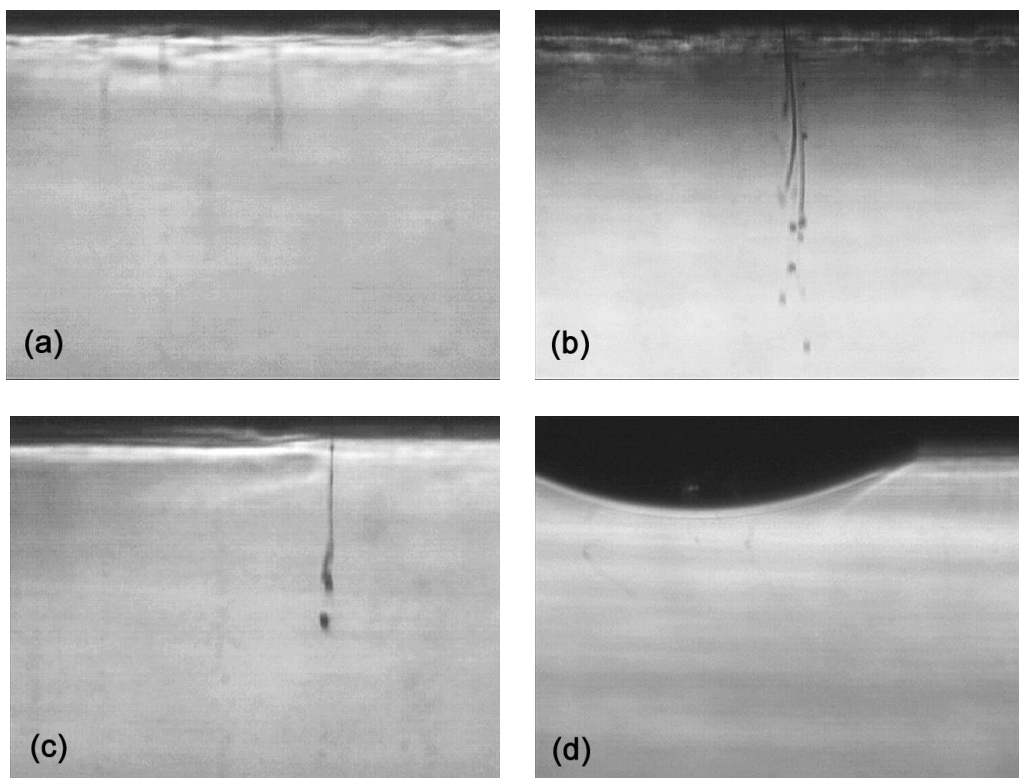


Fig. 11 Fluids emerging from a DOD print head.

(a) PVP-1/S465 ($1.4/0 \text{ mol dm}^{-3}$), (b) PVP-1/S465 ($1.4/0.002 \text{ mol dm}^{-3}$),
(c) PVP-1/S465 ($1.4/0.01 \text{ mol dm}^{-3}$), (d) PVP-63/S465 ($0.135/0.003 \text{ mol dm}^{-3}$)

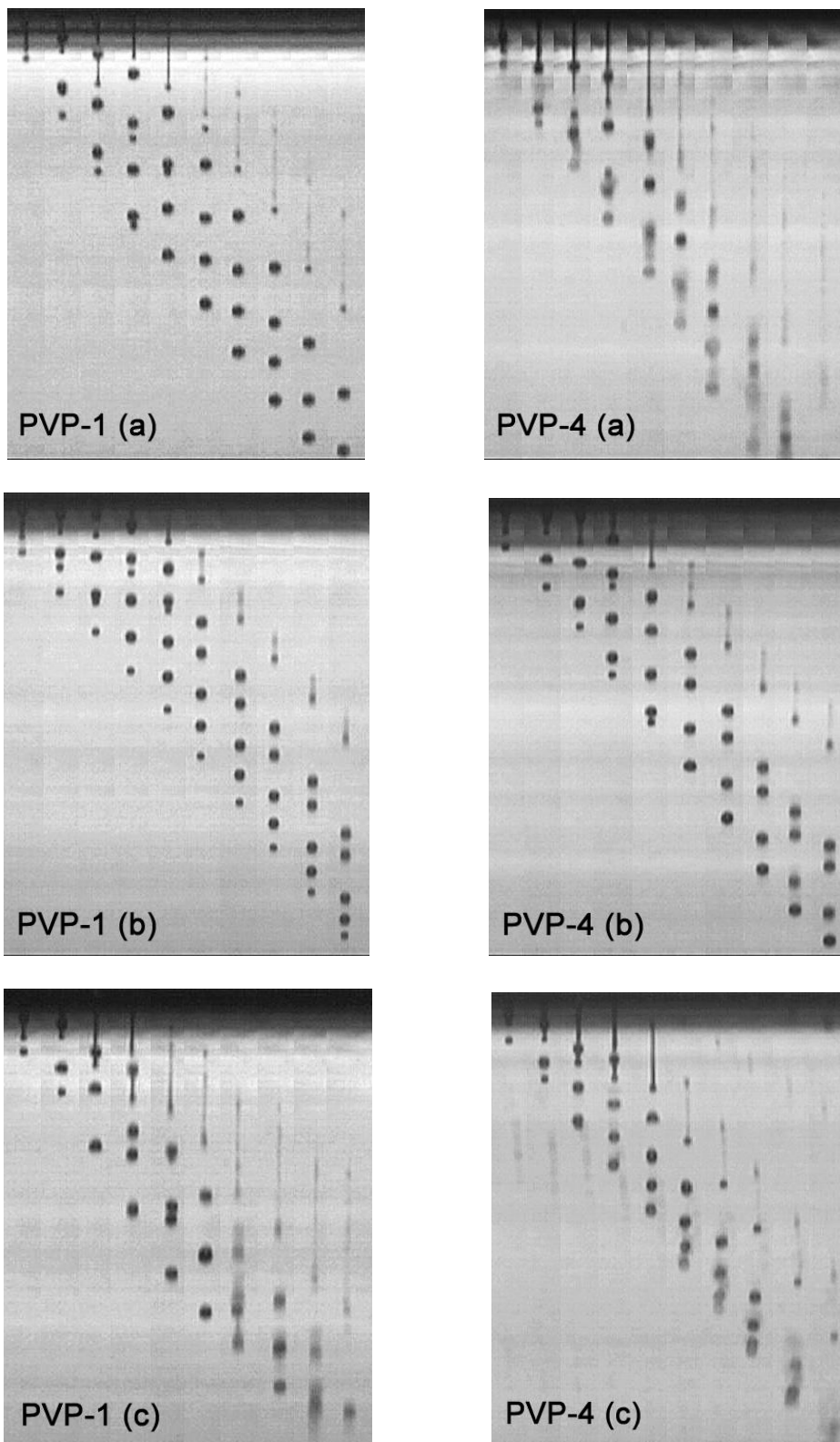


Fig. 12 Generation patterns of inkjet drops of different ink compositions.

PVP-1; 1.4 mol dm^{-3} / S465 (a) 0.003 , (b) 0.004 , (c) $0.005 \text{ mol dm}^{-3}$

PVP-4; 0.7 mol dm^{-3} / S465 (a) 0.003 , (b) 0.004 , (c) $0.005 \text{ mol dm}^{-3}$