

Effects of Polymer Molecular Weight on the Interaction between Acid Dyes and Poly(vinylpyrrolidone) in Inkjet Ink for Textiles

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Abstract: The detailed understanding of the interaction between dyes and additives in the practical service condition is required to develop an inkjet ink for textiles. In the present study, the interaction between three acid dyes (C. I. Acid Red 88, 13, and 27) and a water-soluble polymer, poly(vinylpyrrolidone) (PVP), with different molecular weight was investigated. The binding constants of the dyes with PVP, K_{bind} , were determined by means of the visible absorption spectrum measurements. The K_{bind} values decreased with an increase in the number of sulfonate groups in the acid dyes (an increase in the solubility of the dyes in water). This suggests that the affinity to PVP decreases with increasing water solubility. Furthermore, the binding constants were diminished by increasing molecular weight of PVP. It is presumably due to the conformation change of PVP with molecular weight. For further discussion, the thermodynamic parameters for the binding, viz. the enthalpy change, ΔH_{bind} , and the entropy change, ΔS_{bind} , were determined from the temperature dependence of K_{bind} . The ΔH_{bind} values for all the dyes were negative, showing that the binding processes are exothermic. The absolute values of ΔH_{bind} decreased with the increase in the number of sulfonate groups in the dye molecules. On the other hand, the increase of PVP molecular weight made the thermodynamic process to be less enthalpic and more entropic. Thus, the nature of the interaction should be affected by PVP molecular weight, because the polymer conformation is strongly influenced by the molecular weight.

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1. Introduction

The composition of the inkjet ink for textiles is very complicated due to the complex nature and more challenging requirements [1,2]. The ink must have physicochemical properties which are specific to printing devices [2-5]. Adequate ink composition enables ink jet printing which can realize highly color developed print images and can penetrate into the textiles in a short time to prevent of winding or feathering of the woven fabric after textile printing, and, in addition, ink can be stably stored for a long period of time [2,6,7].

As described in the previous paper [8], an inkjet ink is contained by not only dyes or pigments but also additives, and the types and amounts of additives in the inkjet ink are of significance, since the various types of additives are used to adjust physical properties of ink and used in order to solve the other problems such as various fastness properties, color strength, dye fixation and ink penetration which occur in printing processes [9,10]. Especially, a polymer additive affects the improvement of the water fastness and light fastness since polymers can stabilize and immobilize the dye both physically and

chemically [11-13], though it causes negative effects on print quality [12]. Furthermore, the addition of polymers in inkjet ink improves the durability of ink and prints since the polymers can be soluble in the medium or dispersed, and can be ionic or nonionic [5,14]. Also, to improve the rubbing resistance of prints [23], to improve the binding force of the ink and the fiber [15-17], polymers are used as additives.

Poly(vinylpyrrolidone) (PVP) is a nonionic water-soluble polymer having a hydrocarbon chain with strongly polar side groups [18] which is widely used in various fields such as cosmetic, toiletry, pharmaceutical, adhesive, textile and dyeing [19-22]. PVP has a number of hydrophilic portions and, hence, have high affinity for water molecules, effectively preventing the evaporation of water. Furthermore, it is used to dissolve the precipitates which are produced in a nozzle of a printing head by unfavorable drying : the hydrated form of PVP makes precipitates to disintegrate [23]. The content of the PVP in the print is maintained to be low, because it adversely affects the water fastness of the print [23].

In a previous paper [8], the aggregation behavior of three acid dyes (C. I. Acid Red 88, 13, and 27) containing

different number of sulfonate groups in the absence and presence of PVP was investigated by means of visible absorption spectroscopy. As a result, the higher the solubility of the dyes in water (the larger the number of sulfonate groups in the dyes), the lower are the aggregation constants of the dyes. Furthermore, the aggregation processes of the dyes in the polymer solutions were thermodynamically different from those in water, reflecting the interactions between the dyes and the polymer chains. Therefore, to investigate the adequate inkjet ink for textiles, the elucidation of the interactions between the dyes and the polymer is important.

PVP is known to bind with any one of direct, acid and reactive dyes which have chromophoric centers such as azo, stilbene, phthalocyanine and anthraquinone [24]. The manner of binding is greatly influenced by the substituents, e.g. OH, NH₂, COO⁻, and SO₃⁻, in the dye molecules: the number and position of the substituents determine the binding affinity. The main driving force is ascribed to electrostatic interaction and hydrogen bonding between the dipolar pyrrolidone groups and anionic or polar groups on the dye [24,25].

In a typical inkjet ink for textiles, the water-soluble polymer has a weight-average molecular weight (M_w) between 2,000 to 1,000,000. When the molecular weight is too low, the rubbing resistance of the image cannot be attained. On the other hand, when the molecular weight is too high, the viscosity of the ink may be too high for an inkjet recording system [23]. Therefore, the study on the effects of the polymer molecular weight is worthwhile to improve the inkjet ink.

In the present study, the interaction between the three acid dyes and PVP with different molecular weight was investigated. The binding constants of the dyes with PVP were determined by means of the visible absorption spectrum measurements. Furthermore, thermodynamic parameters were determined from the temperature dependence of the binding constants. From the results, the effects of polymer molecular weight on the interaction between the dyes and PVP are discussed.

2. Experimental

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. R-2 was prepared by the coupling reaction of diazotized 4-amino-1-naphthalenesulfonic acid with sodium

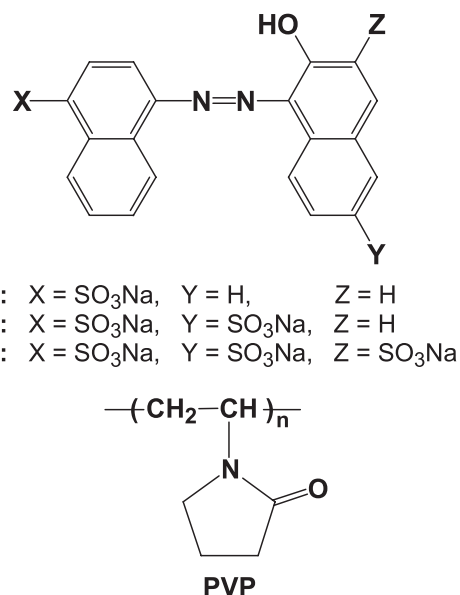


Fig. 1 Chemical structure of the acid dyes and PVP used.

2-hydroxy-6-naphthalenesulfonate under an alkaline condition and purified as described in our previous paper [8].

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

In order to investigate the interaction between the dyes and the polymers, the visible absorption spectra of aqueous solutions having various polymer concentrations (the polymer concentration is expressed on the basis of a monomer mol) and a constant dye concentration (R-1; 2.97 × 10⁻⁵ mol dm⁻³, R-2; 2.81 × 10⁻⁵ mol dm⁻³, R-3; 2.83 × 10⁻⁵ mol dm⁻³) were recorded using a JASCO UV-530 spectrophotometer at 15, 25, 35 and 45 °C.

3. Results and discussion

The effect of successive addition of PVP-1 on the visible absorption spectra of aqueous R-1 solution is represented in Fig. 2. Isobestic points were defined in the polymer concentration region examined. The existence of the isobestic points makes it possible to assume a single equilibrium in the binding process of the R-1/PVP-1 system. The similar spectral changes were also observed for the other dye/PVP systems. The extinction coefficients at the maximum absorption wavelength decreased with increasing PVP concentration for all the dyes. This suggests that the anionic groups (sulfonate groups) of the dyes are believed to interact with the positively charged pyrrolidone rings (pyrrolidone carries

partially positive charge on the nitrogen atom) [26,27], i.e. the electrostatic interaction is effective [28-32].

To analyze the spectral change with PVP-1 concentration, the extinction coefficients, ϵ , at the wavelength (R-1 ; 492 nm, R-2 ; 494 nm, R-3 ; 509 nm) where the largest difference was observed in order to obtain the most accurate values are useful. As shown in Fig. 3, the extinction coefficients decreased with increasing polymer concentration for all the dyes. At the same PVP concentration, the extinction coefficient, ϵ , increased in the order of R-1 < R-2 < R-3.

Fig. 4 shows the plots of the observed extinction coefficients, ϵ , against the logarithm of the PVP concentrations for all the dyes and all PVP's with different molecular weights at 25°C. These extinction coefficients decreased with increasing polymer concentrations and decreasing PVP molecular weight for all the dyes, but the manner of the change varied from dye to dye. The effects of dye structure on the interaction with PVP were much larger than those of the PVP molecular weights.

As was pointed out in Fig. 2, the spectral change for all the dye/PVP systems showed isosbestic points. Therefore, we assumed the following single equilibrium :



where D, P and D·P express the dye, PVP and dye/PVP complex, respectively. From this assumption, equation 2 is derived for determination of the binding constant, K_{bind} , of the dyes and PVP [8, 28-32].

$$\epsilon = \epsilon_f + \frac{\epsilon_b - \epsilon_f}{2C_0} \left\{ A - (A^2 - 4C_0 \cdot C_P)^{1/2} \right\} \quad (2)$$

where C_0 the total dye concentration, C_P the total PVP concentration, ϵ_f the extinction coefficient of the free dye, ϵ_b the extinction coefficient of the bound dye, and $A = C_0 + C_P + 1/K_{\text{bind}}$. On the basis of equation 2, the binding constant, K_{bind} , and the extinction coefficient of the bound dye, ϵ_b , were calculated using the nonlinear least-squares method (SigmaPlot, SPSS Inc.) [8,28-32]. The solid lines in Fig. 3 expresses the fitting curves calculated using K_{bind} and ϵ_b obtained above and shows good agreement with the observed values.

The binding constants, K_{bind} , for all the dyes are given in Table 1. The binding constants of the acid dyes with PVP were dependent on the dye structure. The K_{bind} values decreased with an increase in the number of sulfonate groups in the acid dyes at all temperatures. As was described in previous papers [31,33-35], the

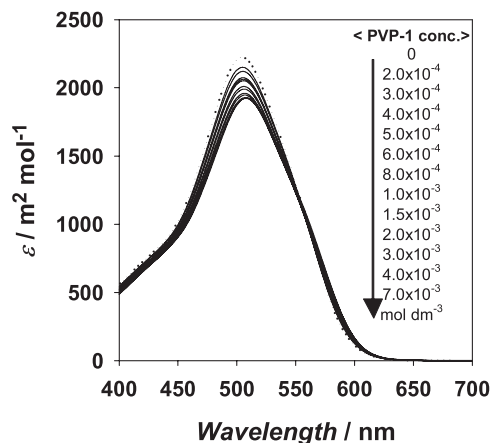


Fig. 2 Visible absorption spectra of aqueous R-1 solutions in the absence and presence of PVP-1 at 25 °C. R-1 concentration is $2.97 \times 10^{-5} \text{ mol dm}^{-3}$.

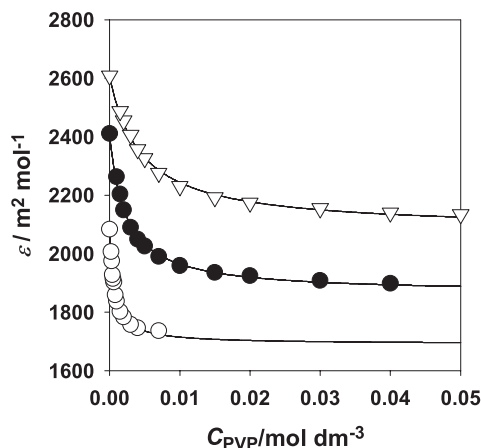


Fig. 3 Dependence of the extinction coefficients on the PVP-1 concentration at 25 °C. ○, R-1 (492 nm); ●, R-2 (494 nm); ▽, R-3 (509 nm). The solid lines show the calculated extinction coefficients.

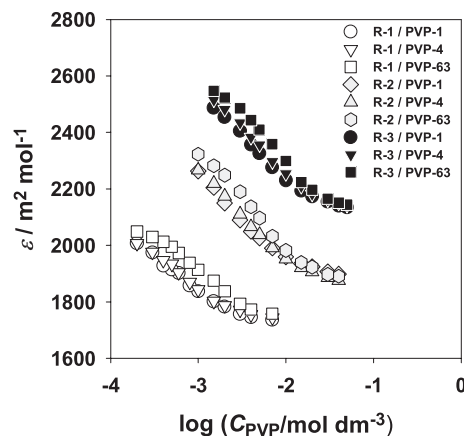


Fig. 4 Dependence of the extinction coefficients on PVP concentration at 25 °C. R-1, 492 nm ; R-2, 494 nm ; R-3, 509 nm.

increasing number of SO_3^- groups diminishes the binding constants. This result shows that the hydrophilic moiety of the dyes greatly affects the interaction. It is worthwhile to mention that the introduction of sulfonate groups into the dye molecule increases the solubility in water, i.e. the solubility increases in the order of $\text{R-1} < \text{R-2} < \text{R-3}$, which corresponds to the decreasing order of K_{bind} ($\text{R-1} > \text{R-2} > \text{R-3}$). The similar tendencies were also observed in the previous studies, in which the binding of the other acid dyes containing different number of sulfonate groups with PVP in aqueous solutions was investigated. The maximum dye binding capacity (mol/kg PVP) with PVP of low molecular weight ($M_w \sim 10,000$), greatly decreased in the order of the C. I. Acid Red 11 $>$ C. I. Acid Red 44 $>$ C. I. Acid Red 18, which is comparable to the increasing order of the number of sulfonate groups [36]. This observation suggests that the binding affinity is influenced by the number of the SO_3^- substituent rather than by the position of them. Furthermore, the effects of the substituents such as trifluoromethyl, methyl, and sulfonate groups on the binding of the acid dyes with PVP were investigated in detail [34,35]. In the papers, six acid dyes, sodium 1-phenylazo-2-hydroxy-6-naphthalenesulfonate, sodium 1-(3-trifluoromethylphenylazo)-2-hydroxy-6-naphthalene sulfonate, sodium 1-(3-methylphenylazo)-2-hydroxy-6-naphthalenesulfonate, disodium 1-phenylazo-2-hydroxy-3,6-naphthalenedisulfonate, disodium 1-(3-trifluoromethylphenylazo)-2-hydroxy-3,6-naphthalenedisulfonate, and disodium 1-(3-methylphenylazo)-2-hydroxy-3,6-naphthalenedisulfonate were used. The increasing number of sulfonate groups also diminished the binding constants in these studies. Furthermore, the introduction of the trifluoromethyl group decreased the binding constants,

while the presence of the methyl group showed the opposite behavior. Therefore, the former dyes are more hydrophobic than the latter. Thus not only ionic groups but also alkyl or fluoroalkyl groups affect the binding constants of the acid dyes with PVP. This should be due to the change in the hydrophobicity or hydrophilicity of the dyes by the substituent. In addition, similar tendency was observed for the other acid dye molecules such as methyl orange, its homologues [26,37-42], azo dyes having different chain length of alkyl groups [28], fluorinated azo dyes [34,37,43], and so on [29-32].

For all the dyes used in the present study, the binding constants decreased with an increase in PVP molecular weight. This result should be explained as follows. The molecular weight is strongly concerned with the conformation of the polymer chain in aqueous solutions. In the previous studies, the binding affinity of acid dyes with PVP was connected to the conformational change of the polymer [35,39]. PVP has a more compact conformation in the presence of NaCl and LiCl, whereas the polymer chain has a highly swollen, extended, and unfolded conformation in aqueous NaSCN solutions and phosphate buffer, as evidence from the high intrinsic viscosity. The binding constants of the acid dyes with PVP having compact conformation were smaller than those with the polymer having unfolded conformation [35,39,44]. The fact that the folded conformation makes the binding affinity to be smaller suggests that the PVP with higher molecular weight might form the folded conformation. On the other hand, the anionic groups (sulfonate groups) of the dyes are believed to interact with the positively charged pyrrolidone rings (pyrrolidone carries partially positive charge on the nitrogen atom [26,27]). This electrostatic interaction is influenced by the

Table 1 The binding constants ($\text{dm}^3 \text{mol}^{-1}$) of the dyes with PVP.

| | 15°C | 25°C | 35°C | 45°C |
|--------|------------|------------|-----------|----------|
| R-1 | | | | |
| PVP-1 | 2100 ± 200 | 1570 ± 100 | 1120 ± 70 | 730 ± 60 |
| PVP-4 | 1950 ± 170 | 1480 ± 100 | 1060 ± 40 | 690 ± 30 |
| PVP-63 | 780 ± 90 | 630 ± 60 | 480 ± 40 | 380 ± 30 |
| R-2 | | | | |
| PVP-1 | 590 ± 30 | 450 ± 20 | 327 ± 14 | 238 ± 12 |
| PVP-4 | 464 ± 15 | 357 ± 9 | 277 ± 7 | 204 ± 9 |
| PVP-63 | 266 ± 19 | 208 ± 14 | 165 ± 11 | 125 ± 7 |
| R-3 | | | | |
| PVP-1 | 298 ± 15 | 230 ± 10 | 179 ± 7 | 132 ± 4 |
| PVP-4 | 227 ± 17 | 180 ± 12 | 139 ± 8 | 109 ± 6 |
| PVP-63 | 132 ± 13 | 110 ± 10 | 87 ± 7 | 70 ± 5 |

conformation of a dissolved polymer chain in aqueous solutions. If the polymer has a compact conformation, the cationic loci are hardly exposed to water and the electrostatic interaction is hindered. Thus dye molecules are hard to incorporate into the more compact polymer chain, therefore, the binding constants are diminished by increasing molecular weight of PVP. The hydrophobic interaction is favored in the compact conformation, whereas the electrostatic interaction is favorable in the unfolded state, as described in the previous papers [39,44].

However, the various effects of the molecular weight on the binding of dyes with PVP are reported in previous studies. In the case of C. I. Direct Red 81 and C.I. Direct Blue 15, the binding affinity of the dyes with PVP with Mw ~ 9,300 was smaller than that with PVP with Mw ~ 42,500, which was about as efficient as PVP with Mw ~ 1,100,000 [45]. In case of the C. I. Fluorescent Brightener 30, C. I. Fluorescent Brightener 32 [46, 47], C. I. Vat Yellow 1, and C. I. Vat Yellow 2 [48], the extent of interaction did not depend on the molecular weight, whose range was 10,000 - 750,000. The monosulfonated dye, C. I. Acid Red 11, showed increasing maximum dye binding capacity when the molecular weight was increased from 10,000 to 47,000, while in the case of di- and trisulfonated dyes, C. I. Acid Red 44 and C. I. Acid Red 18, showed no further increase beyond 38,000 of the molecular weight [36]. These results suggest that the maximum dye binding capacity as well as the binding affinity of the dyes with PVP depends on the molecular weight. Furthermore, the binding affinity should be dependent upon the concentration of aqueous PVP solutions, because the conformation of PVP chains changes with the PVP concentration. The PVP concentrations used in the present study are different from those applied in the previous papers and this fact is concerned with the distinction in the effects of the molecular weight on the binding affinity of the dyes with PVP. Thus, it is found that the molecular weight is one of the most important factors to determine the binding affinity of the dyes with PVP together with the dye chemical structures.

For further discussion, the thermodynamic parameters, the enthalpy change, ΔH_{bind} , and the entropy change, ΔS_{bind} , were determined from the temperature dependence of K_{bind} , using equation 3 :

$$\ln K_{\text{bind}} = -\frac{\Delta H_{\text{bind}}}{R} \cdot \frac{1}{T} + \frac{\Delta S_{\text{bind}}}{R} \quad (3)$$

where T is the absolute temperature and R is the gas constant. ΔH_{bind} and ΔS_{bind} were calculated from the plot of

$\ln K_{\text{bind}}$ against $1/T$ (van't Hoff plot) (Fig. 5), and are summarized in Table 2.

The ΔH_{bind} values for all the dyes were negative, showing that the binding processes are exothermic. The absolute values of ΔH_{bind} decreased in the order of R-1 > R-2 > R-3, which is comparable to the order of the number of sulfonate groups. This suggests that the enthalpy change is concerned with the solubility of the dyes, i.e. the hydrophilic-hydrophobic balance of the dyes contributes to the enthalpy change, and the same tendency was shown in the previous paper [31]. The ΔS_{bind} values did not show a tendency with increasing number of sulfonate groups. This might be due to the complicity in dehydration of hydrated water around the dyes and PVP.

On the other hand, the increase of PVP molecular weight made the thermodynamic process to be less enthalpic and more entropic. This result supports that the higher molecular weight makes the conformation to be compact coil structure leading to the hindrance of the

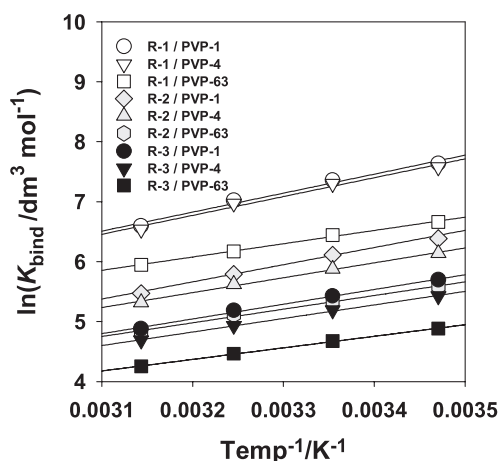


Fig. 5 Van't Hoff plots ($\ln K_{\text{bind}}$ vs. $1/T$) for the binding of the dyes with PVP.

Table 2 Thermodynamic parameters for the binding of the dyes with PVP.

| | ΔH_{bind} (kJ mol ⁻¹) | ΔS_{bind} (J mol ⁻¹ K ⁻¹) |
|--------|---|--|
| R-1 | | |
| PVP-1 | -26 ± 2 | -28 ± 8 |
| PVP-4 | -26 ± 3 | -27 ± 8 |
| PVP-63 | -18.4 ± 0.7 | -8 ± 2 |
| R-2 | | |
| PVP-1 | -23.3 ± 1.1 | -28 ± 4 |
| PVP-4 | -20.7 ± 1.0 | -21 ± 3 |
| PVP-63 | -18.9 ± 0.9 | -19 ± 3 |
| R-3 | | |
| PVP-1 | -20.4 ± 1.0 | -24 ± 3 |
| PVP-4 | -18.8 ± 0.5 | -20.0 ± 1.8 |
| PVP-63 | -16.0 ± 0.5 | -15.0 ± 1.5 |

electrostatic interaction. The compact conformation is believed to form a less hydrophilic environment, which probably interacts with the hydrophobic part of the dye molecules with release of the hydrated water, thus resulting in more entropic binding as was described in a previous paper [35]. Therefore, the compact conformation increases the contribution of hydrophobic interactions. The above results suggest that the PVP chain conformation changes from an extended coil at low molecular weight to a compact coil at high molecular weight.

To make sure what binding processes are concerned with the acid dye/PVP systems, the compensation relationship between ΔH_{bind} and ΔS_{bind} [49,50] is useful. Fig. 6 shows the ΔH_{bind} vs. ΔS_{bind} plots for the complex formation between three acid dyes and PVP's with different molecular weight. The compensation relationship between ΔH_{bind} and ΔS_{bind} differed among the three dyes. However, in the case of each dye, the plots of ΔH_{bind} against ΔS_{bind} lie on each straight line for the different PVP's. This fact might suggest that the binding processes are influenced by the dye structure rather than the molecular weight of PVP. Thus, it is concluded that the binding constants are influenced by both the dye structure and the molecular weight of PVP, but the manner of the binding is affected only by the dye structure.

4. Conclusions

The binding behavior of the acid dyes with PVP in aqueous solutions depends on the molecular weight of PVP as well as the dye structure. The higher the solubility of the acid dyes in water (the larger the number of sulfonate groups in the dyes), the lower the binding

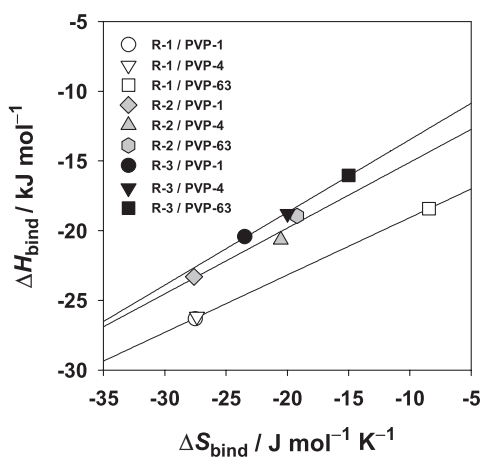


Fig. 6 Compensation relationship between ΔH_{bind} and ΔS_{bind} .

affinity to PVP, indicating that the electrostatic interaction is strongly concerned with the binding process. Furthermore, the polymer molecular weight affected the interaction between the dyes and PVP. As the higher molecular weight makes the conformation to be compact, the binding constants are diminished by increasing molecular weight of PVP.

The ΔH_{bind} values are concerned with increasing number of sulfonate groups, whereas, the ΔS_{bind} values did not show a tendency with the solubility of the dyes. Also the increase of PVP molecular weight made the thermodynamic process to be less enthalpic and more entropic. This result supports that the higher molecular weight makes the conformation to be compact leading to the hindrance of the electrostatic interaction. The compensation relationship between ΔH_{bind} and ΔS_{bind} shows that the binding processes are influenced by the dye structure rather than the molecular weight of PVP.

The above results suggest that not only the dye structure but also the molecular weight of PVP influences the interaction between the dyes and PVP in aqueous solutions. The consideration of this fact makes it possible to prepare the adequate inkjet ink.

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