

## Interaction between anionic dyes and cationic flocculant P(AM-DMC) in synthetic solutions

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### Abstract

Copolymer of acrylamide and 2-[(methacryloyloxy)ethyl]trimethylammonium chloride [P(AM-DMC)] is found to be effective to combine anionic dyes with strong aqueous solubility. This work aims mainly at revealing the interaction between anionic dyes and [P(AM-DMC)] by running jar test, spectra analysis and equilibrium dialysis experiments. The results show that P(AM-DMC) effectively decolorizes the tested strong water soluble anionic dyes, such as acidic, reactive and direct dyes, from their aqueous solutions under mild acidic and neutral conditions. Higher cationicity and optimal dose of flocculant P(AM-DMC) have to be used to achieve satisfactory and effective decolorization. Comparison of IR spectra of dye, flocculant P(AM-DMC) and the floc formed indicates chemical interaction occurred between sulfonic groups of dye and quaternary ammonium of flocculant. Plots of  $r-\log C$  suggest cooperative interaction exists evidently for some dyes tested. Addition of KCl or urea reduces binding extent evidently, which shows the importance of electrostatic and hydrophobic interaction. Therefore the interaction between dyes tested and P(AM-DMC) might be controlled by hydrophobic, cooperative interaction and energetic interaction which includes chemical and electrostatic interactions.

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**Keywords:** Energetic interaction; Hydrophobic interaction; Anionic dye; Flocculation; Equilibrium dialysis

### 1. Introduction

Studies of the interaction between anionic dyes and synthetic polymers in solutions have been carried out extensively. The most studied systems are polyvinylpyrrolidone-methyl orange (MO) and its homologs [1], polyethylenimine-azo dyes [2], poly(2-diethylaminoethyl methacrylate)-MO and its homologs [3], 2-hydroxyethyl methacrylate-*N*-vinyl-2-pyrrolidone copolymer-MO and its homologs [4], polyvinylpyrrolidone-azo dyes [5] and PAN-DCD dyes [6,7]. These studies showed that the binding mechanism of dyes by polymers could be described as either hydrophobic or electrostatic interaction. The formation, structure and application of complexes of polyelectrolytes and ionic dyes were reviewed in [8].

We found that copolymer of acrylamide and 2-[(methacryloyloxy)ethyl]trimethyl ammonium chloride [P(AM-DMC)] is an effective reagent to react with strong water soluble anionic dyes while flocculants are screened for optimal decolorization experiments of dye aqueous samples [9]. P(AM-DMC) is an amphiphilic cationic polyelectrolyte containing both hydrophobic groups (methyl groups and backbone chain) and hydrophilic groups (positively charged tertiary amine and acrylamide groups). Griebel et al. [10,11] has characterized its solution properties and structure–property relationships. There are many reports on using this copolymer as primary flocculant or flocculant aid in clarification of industrial wastewater, separation of solid–liquid systems, dewatering of sludge, and so forth [12–14]. However, to our knowledge, studies on its application in decolorization of water-soluble anionic dyes were rare [9], and no report on its binding mechanism to dyes was found.

In the present study, we investigate the reactive extents of P(AM-DMC) with strong water soluble anionic dyes and the binding mechanism between P(AM-DMC) and dyes by

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### Nomenclature

$C$	molar concentration of free dye in solution
$D$	total molar concentration of dye
DE	decolorization efficiency of dye by P(AM-DMC)
$P$	total molar concentration of the polymer quaternary ammonium sites
$r$	the number of moles of dye bound per $10^5$ g of polymer
$[\eta]$	intrinsic viscosity of flocculant
$\tau$	cationicity of flocculant

performing jar test, spectra analysis and equilibrium dialysis experiments.

## 2. Materials and methods

### 2.1. Chemicals

DMC {2-[(methacryloyloxy)ethyl]-trimethylammonium chloride}, as a 76% aqueous solution supplied by Xinyu Co. Ltd., was used without further purification. Acrylamide (AM), potassium persulfate ( $K_2S_2O_8$ ), urea and ethylenediamine tetraacetic acid tetrasodium salt ( $Na_4EDTA$ ) were of analytical grade. Potassium poly(vinyl sulfate) (PVSK) was obtained from Wako Pure Chemical Industries, Ltd. Toluidine blue (TBO) was obtained from Shanghai Chemical Reagent Corporation. Dyes tested are strong water-soluble anionic dyes widely used in Tianjin of China. These dyes had a high affinity for flocculant P(AM-DMC). They are all commercial products and used without purification, their characteristics are shown in Table 1.

### 2.2. Synthesis and characterization of P(AM-DMC)

P(AM-DMC) was synthesized with  $K_2S_2O_8$ -urea as initiator at  $45^\circ C$  for 5 h under nitrogen atmosphere in aqueous solution. The intrinsic viscosity  $[\eta]$  of the copolymer in  $1 \text{ mol L}^{-1}$  NaCl solution was measured with an Ubbelohde type viscometer at  $30 \pm 0.05^\circ C$ . The cationicity  $\tau$  of P(AM-DMC) was determined by the colloid titration method [15]. For the titration of cationic polymers,  $1/400 \text{ mol L}^{-1}$  PVSK was used as the titrant and 1% toluidine blue was used as the indicator.

### 2.3. Flocculated decolorization of dyes

The flocculated decolorization tests of dyes by P(AM-DMC) were run on a TS6 jar tester at room temperature ( $21\text{--}23^\circ C$ ). The dye solutions ( $50 \text{ mg L}^{-1}$ ) were prepared by dissolving the dyes into distilled water. Calibration curves were made for each dye at its absorbance maximum. Various amounts of 0.1% (w/v) flocculant solution were added into 250 mL beakers containing 200 mL dye solution. Then the mixed samples were rapidly stirred at 200 rpm for 2 min, slowly stirred at 50 rpm for the next 10 min. Various sized flocs settled in different velocity and there was not a visible solid-liquid interface. Most of flocs settled on bottom of the beaker within 30 min. However, smaller flocs suspended in liquid need more time to settle. The time needed for complete settlement lay on the type of dye tested, which ranged from 3 to 12 h. Therefore, the flocculant-treated solutions were left overnight to complete the sedimentation process and the supernatant samples were withdrawn from a level 1–2 cm below the surface to measure residual dye concentration. The sludge volume ranged from 0.4 to 3 mL in a 200 mL tested dye solution, and changed with different dyes.

The dye concentration in supernatant was determined from absorbance measurements by using a spectrophotometer as described in Section 2.5. In pH influence experiments, the pH of dye solutions was adjusted to different values with hydrochloric acid and sodium hydroxide solution before flocculant addition and stirring. The decolorization efficiency (DE) was calculated by following equation,

$$DE\% = \left(1 - \frac{CV}{C_0V_0}\right) \times 100$$

where  $C$  and  $C_0$  denote the dye concentration in the solution after and before flocculation,  $V$  and  $V_0$  are the volume of solution after and before flocculation, respectively.

### 2.4. Equilibrium dialysis

Extent of the binding of dyes by P(AM-DMC) was measured by equilibrium dialysis technique in 100 mL buffer solution containing  $0.1 \text{ mol L}^{-1}$  potassium dihydrogen phosphate and sodium hydroxide (pH 6). The molecular weight cutoff of dialysis bag is 8000–12,000 Da. A 10 mL aliquot of 0.05% (w/v) polymer inside the dialysis bag was in equilibrium with 15 mL

Table 1  
Characteristics of tested dyes

Name of dye (abbreviation)	Color index	$\lambda_{\text{max}}$ (nm)	Molecular weight
Direct light resistant black G (DG)	Direct black 19 (35255)	650	839
Acid red B (AB)	Acid red 14 (14720)	515	502
Acid mordant black PV (PV)	Mordant black 9 (16500)	530	382
Acid anthraquinone blue (AAB)	Acid blue 25 (62055)	605	411
Acid mordant brown RH (RH)	Mordant brown 33 (13250)	440	375
Reactive brilliant blue KN-R (KN-R)	Reactive blue 19 (61200)	595	627
Reactive flavine yellow K-6G (K-6G)	Reactive yellow 2 (18972)	404	872
Reactive brilliant orange K-GN (K-GN)	Reactive orange 5	476	876
Reactive brilliant red X-3B (X-3B)	Reactive red 2 (18200)	536	615
Reactive black K-BR (K-BR)	Reactive black 8	580	708

of the dye solutions of different concentrations for 48 h, after that the dye concentration outside of the dialysis bag did not change. The dialysis bag was almost submerged into the buffer solution, but its two sides were above the buffer surface. Control tubes contained only buffer inside the dialysis bag. Experiments were carried out at 20 °C. Equilibrium dye concentration was determined as described in Section 2.5.

## 2.5. Measurements

Dye concentrations were determined from absorbance measurements by using a 752 spectrophotometer, according to the concentration–absorbance standard curves of different dyes at their respective maximum absorption wavelengths. The pH value of solution was measured by using a PHS-3C pH-meter. IR spectra were recorded with Nicolet MAGNA-560 FTIR spectrometer (KBr pellets). UV–vis spectra were determined with Varian CARY 50 Conc UV–vis spectrophotometer.

## 3. Results and discussion

### 3.1. Decolorization efficiency and its influencing factors

#### 3.1.1. Effects of dose, cationicity and intrinsic viscosity of P(AM-DMC) on the DE of dyes

As an example, Fig. 1 illustrates the effects of dose, cationicity and intrinsic viscosity of flocculant on the DE of dye K-BR and DG. DE increases first and then decreases with increasing dose of P(AM-DMC). There is an optimal flocculant dose existed for each dye and flocculant with certain cationicity and intrinsic viscosity. The optimal dose of flocculant having higher cationicity can cause an almost complete decolorization of dyes. But destabilization takes place by the electrostatic repulsion among the anions of dye already bound with polycations when the optimal range is exceeded [16].

Comparison of DE of dyes by four flocculants with different intrinsic viscosity  $[\eta]$  and cationicity  $\tau$  is also shown in Fig. 1. The result indicates that  $[\eta]$  has little influence on the DE of K-BR and DG. The maximum decolorization efficiencies of the dyes are similar when cationicity exceeds 0.52. The greater the flocculant cationicity is, the smaller the optimum dose is. So the flocculant of  $[\eta]$  461 mL g<sup>-1</sup> and  $\tau$  0.60 is used in the following experiments for convenience.

#### 3.1.2. Effect of pH on the DE of dyes

The effect of pH on the decolorization of different dyes by P(AM-DMC) is shown in Fig. 2. It can be seen that the dyes studied have better DE under mild acidic and neutral conditions. That is because that the quaternary ammonium groups in the side chain of P(AM-DMC) are stably charged under mild acidic and neutral conditions, but they are partially neutralized in alkaline medium. On the other hand, too much H<sup>+</sup> and acid radical screened the opposite charges of macromolecule and dye, which make both DE and the binding of dye to P(AM-DMC) decrease in strong acid medium. Therefore, sulfonic groups in dye molecule could react better with quaternary ammonium groups of polymer chain in mild acidic and neutral conditions than they could in alkaline medium.

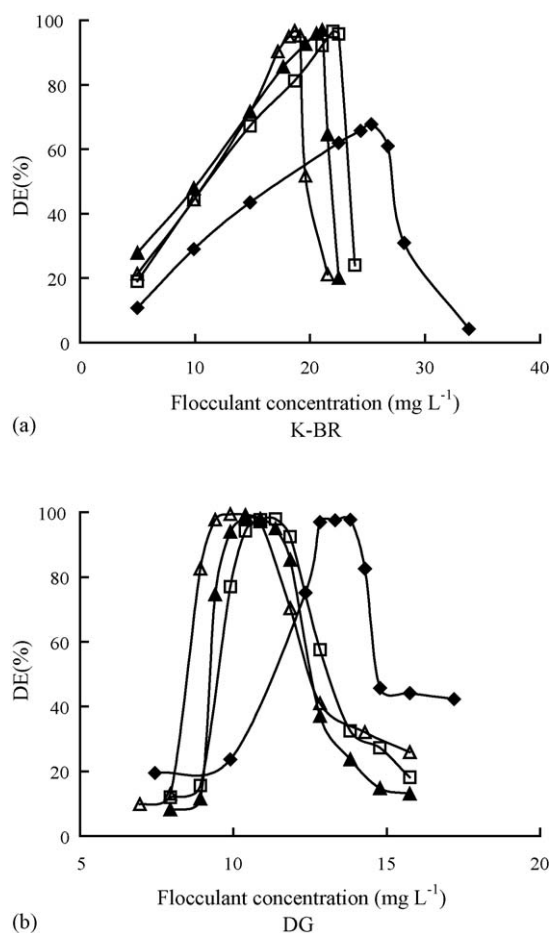


Fig. 1. Effects of dose, cationicity and intrinsic viscosity of P(AM-DMC) on the decolorization efficiency (DE) of dye K-BR and DG: (◆)  $[\eta] = 847 \text{ mL g}^{-1}$ ,  $\tau = 0.32$ ; (□)  $[\eta] = 593 \text{ mL g}^{-1}$ ,  $\tau = 0.52$ ; (▲)  $[\eta] = 461 \text{ mL g}^{-1}$ ,  $\tau = 0.60$ ; (△)  $[\eta] = 343 \text{ mL g}^{-1}$ ,  $\tau = 0.76$ .

### 3.2. Interactions between dye and reactive groups of flocculant

In order to investigate the chemical interaction between P(AM-DMC) and dyes, the IR spectra of P(AM-DMC), X-

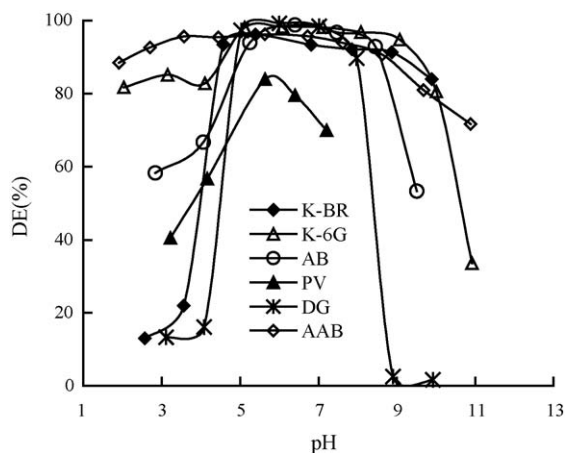


Fig. 2. Effect of pH on the decolorization efficiency (DE) of dyes.

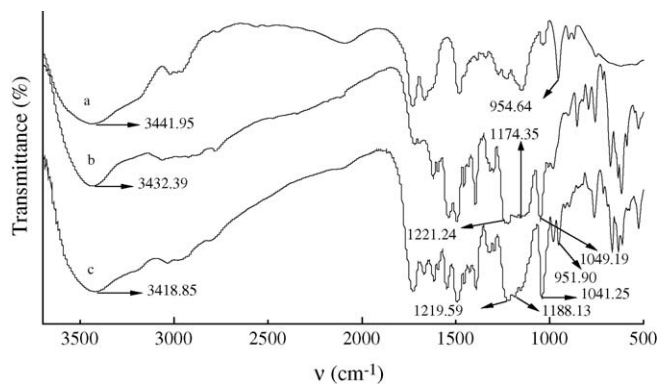


Fig. 3. FTIR spectrum of (a) P(AM-DMC), (b) X-3B and (c) floc formed.

3B and the floc formed are compared in Fig. 3. The band of quaternary ammonium of P(AM-DMC) at  $954.64\text{ cm}^{-1}$  is weakened in intensity and slightly shifted to lower  $951.9\text{ cm}^{-1}$  in the formed floc. Bands assigned to sulfonic group at  $1049.19$ ,  $1174.35$  and  $1221.24\text{ cm}^{-1}$  in the spectrum of X-3B shifted to  $1041.25$ ,  $1188.13$  and  $1219.59\text{ cm}^{-1}$  in floc. These changes indicate sulfonic groups in dye molecules reacted with quaternary ammonium of flocculant and product like  $-\text{N}^+(\text{CH}_3)_3\text{SO}_3^-$  in aqueous solution formed [17]. This is in agreement with the effect of pH on the DE of dyes.

Upon the addition of P(AM-DMC), the X-3B solution exhibits absorption spectral changes in visible region. Fig. 4 illustrates the absorption spectral changes of a  $8 \times 10^{-5}\text{ mol L}^{-1}$  solution of X-3B in the presence of P(AM-DMC) at different  $P/D$  values, where  $P$  is the total molar concentration of the polymer quaternary ammonium sites and  $D$  is the total molar concentration of dye. Two new absorption maxima appear in the visible absorption spectrum after the addition of the flocculant: bathochromic shifts at  $519$  and  $556\text{ nm}$  compared to  $512$  and  $536\text{ nm}$ , the characteristic maxima of the free dye X-3B. The band intensity at  $519\text{ nm}$  was higher than that at  $556\text{ nm}$ .

The spectral changes reflect the interaction between polymer and dyes. These shifts probably are caused by electrostatic

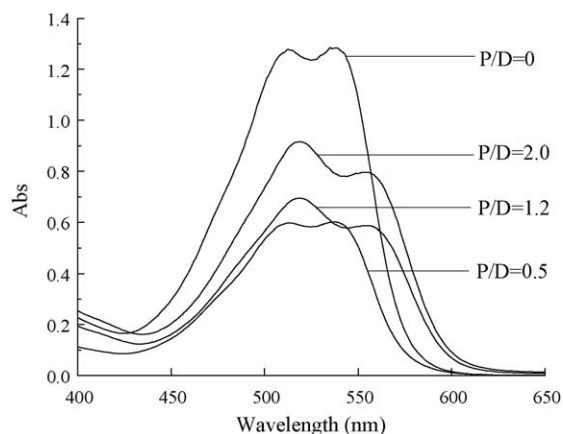


Fig. 4. Absorption spectral changes of X-3B solution ( $8 \times 10^{-5}\text{ mol L}^{-1}$ ) in the presence of P(AM-DMC) at different  $P/D$  values.

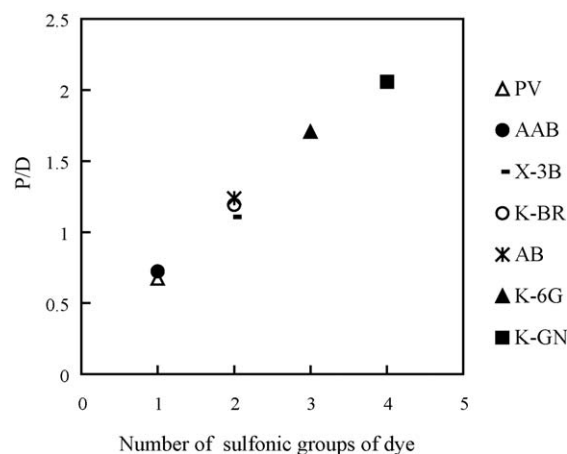


Fig. 5. Relationship between sulfonic group number in dye molecule and  $P/D$  value at which ratio maximum decolorization efficiency reached. The relationship is significant at the 0.01 level (Pearson correlation is 0.997).

interaction and hydrophobic interaction of dye molecule and the polyion [18]. Chmilenko et al. [19] thought the electrostatic interaction plays the determining role.

### 3.3. Electrostatic interaction

To realize electrostatic interaction between anionic groups in dye molecule and quaternary ammonium groups in polymer chain, relationship between sulfonic group number of dye and  $P/D$  value at which ratio maximum decolorization efficiency reached is revealed by analyzing the flocculated experimental data. The results are presented in Fig. 5. Dye PV and AAB have one sulfonic group, the value of  $P/D$  is about 0.7. Dye X-3B, K-BR and AB all have two sulfonic groups,  $P/D$  values range from 1.1 to 1.2. Dye K-6G and K-GN have three and four sulfonic groups, their  $P/D$  values are 1.7 and 2.1 respectively. The value of  $P/D$  increases linearly with increasing numbers of sulfonic group in dye molecule. To further analyze the linear relationship between the number of sulfonic group of dye and  $P/D$  value, the SPSS Software is used to calculate the correlation coefficient. The relationship is significant at the 0.01 level (Pearson correlation is 0.997), which suggests that electrostatic interaction between dye and flocculant plays important role in flocculated decolorization processes.

To further examine the electrostatic interaction between dye and P(AM-DMC), equilibrium dialysis experiment was performed. The binding isotherm of P(AM-DMC) to dye is expressed as  $r$  (the number of moles of dye bound per  $10^5\text{ g}$  of polymer matrix) as a function of the molar concentration of free dye in solution  $C$  to facilitate a comparison of different dyes.

As shown in Fig. 6, the binding extent of dye KN-R by polymer is higher than that of AAB. Dye KN-R and AAB both have the same parent structure and the only difference between them is the number of sulfonic groups. Dye KN-R has an additional  $-\text{SO}_3\text{Na}$  group in its molecule compared to dye AAB molecule. Therefore it seems reasonable to attribute the difference in the

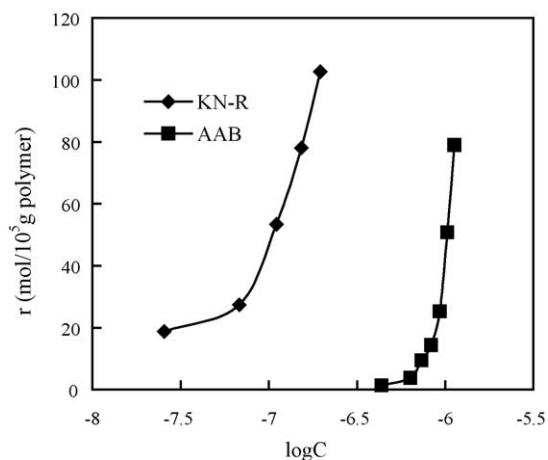


Fig. 6. Binding extent of dye KN-R and AAB by P(AM-DMC) in  $\text{KH}_2\text{PO}_4$ -NaOH buffer, pH 6.0 at 20 °C.

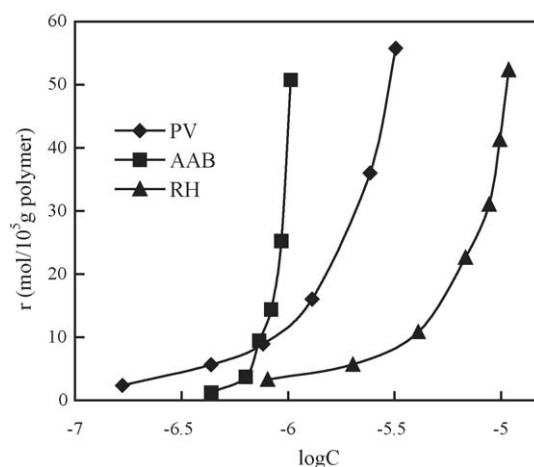


Fig. 8. Binding extent of dye AAB, PV and RH by P(AM-DMC) in  $\text{KH}_2\text{PO}_4$ -NaOH buffer, pH 6.0 at 20 °C.

binding affinity of these dyes to the electrostatic force between dye and polymer.

Some previous studies [16,20,21] reported that the presence of inorganic electrolytes screens the charged groups of polymer and consequently decreases electrostatic interactions between polycations and anionic dyes. To investigate the contribution of the electrostatic force between P(AM-DMC) and dyes, the binding extent is measured in buffered solution and in the presence of added KCl. The results are displayed in Fig. 7. The binding extent of dye X-3B and AAB by the polymer is definitely weakened by the addition of 0.1 mol L<sup>-1</sup> KCl, compared to that in the buffered solution. Moreover, the ability of dye X-3B to bind polycation decreases more than that of dye AAB. Dye AAB only has one sulfonic group, the electrostatic force of which is less than that of dye X-3B that has two sulfonic groups. These results indicate that the electrolytes reduce the extent of binding, hence the binding energy, probably because of a diminished electrostatic interaction between the dye anion and the oppositely charged group on the polymer.

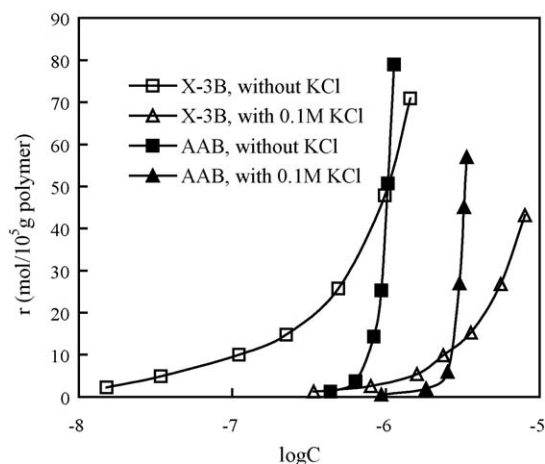


Fig. 7. Effect of KCl on the binding extent of dye X-3B and AAB by P(AM-DMC) in  $\text{KH}_2\text{PO}_4$ -NaOH buffer, pH 6.0 at 20 °C.

### 3.4. Hydrophobic interaction

Dye AAB, PV and RH all have one sulfonic group linked to their molecular structures, but the number of aromatic rings in their molecular structures is different. They have an anthraquinone ring, a naphthalene ring and a benzene ring respectively connected to benzene ring. As displayed in Fig. 8, the binding sequence of the three dyes by the flocculant is anthraquinone ring (AAB) > naphthalene ring (PV) > benzene ring (RH), which is in the order of increasing volume of nonpolar portion. The bigger the volume of the aromatic ring is, the greater the binding force of the dye is. Thus it is likely that the hydrophobic interaction also plays a significant role in the binding of dye by polycation since the ionic contributions are the same among the three dyes.

Urea was examined for its effect on the binding of dyes by P(AM-DMC). The result is presented in Fig. 9. Clearly the addition of urea decreases the binding affinity of the polymer toward the dyes. In the presence of 2 mol L<sup>-1</sup> urea, the ability of P(AM-DMC) to bind X-3B and AAB is strongly suppressed. Binding

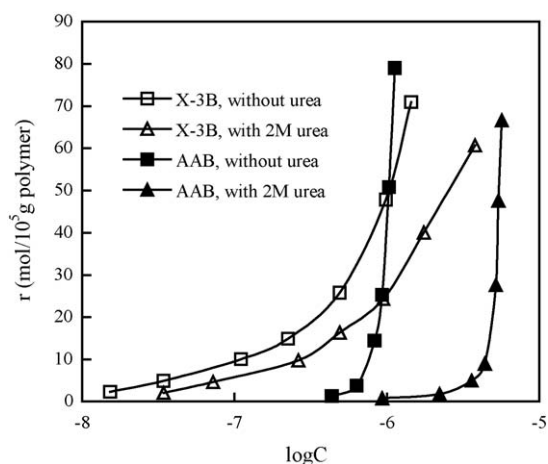


Fig. 9. Effect of urea on the binding extent of X-3B and AAB by P(AM-DMC) in  $\text{KH}_2\text{PO}_4$ -NaOH buffer, pH 6.0 at 20 °C.

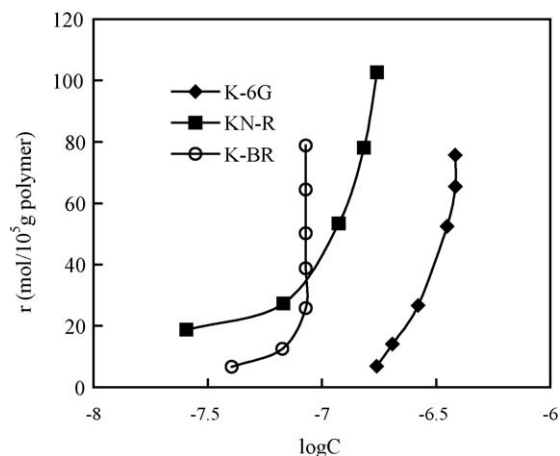


Fig. 10. Relationship of  $r$  and  $\log C$  for K-6G, KN-R and K-BR in  $\text{KH}_2\text{PO}_4$ -NaOH buffer, pH 6.0 at  $20^\circ\text{C}$ .

ability of AAB declines more than that of X-3B. The most likely explanation for this effect of urea is that it disrupts the structure of the aqueous environment, hence lowers the tendency of non-polar groups of dyes and polymers to participate in hydrophobic interaction [7,22]. The dye AAB has an anthraquinone ring in its molecular structure, which is bigger than naphthalene ring of X-3B in volume, therefore enhanced hydrophobic interaction. These results again demonstrate that the binding of dyes by the flocculant P(AM-DMC) includes not only the energetic interaction but also the hydrophobic interaction between nonpolar components.

### 3.5. Cooperative interaction

As shown in Figs. 6–9, the most striking feature of AAB is the steep rise in binding with increasing concentration of dye, which suggests cooperative interaction in this binding. Thus the binding does not follow the Langmuir isotherm. Such cooperative binding isotherm produced by P(AM-DMC) is a manifestation of the stacking (i.e., interaction with one another) of neighboring dye molecules bound on the polymer flocculant. The  $\pi$ -electron interaction mentioned in Section 3.2 is probably one type of interactions between bound dyes and thus may be one possible reason for the cooperative binding. The dye tends to bind cooperatively and stack readily on the polymer matrix at higher dye concentrations. Therefore, the Klotz plots [23] (the double reciprocal plots,  $1/r$  versus  $1/C$ ) do not show a linear relation on the entire free cosolute concentration range. This cooperative binding has been revealed by Takagishi et al. [2,22,24], who found that cooperativity is evident in flocculating systems of PEI-azo dye or polyion-methyl orange when dye concentrations increases.

Obvious deviations from linearity of the  $1/r$  versus  $1/C$  plot also appear in the binding of other dyes such as K-6G, KN-R and K-BR (Fig. 10). So we believe cooperative interaction caused by the bound dye–dye interaction also contributes to the binding mechanism of anionic dyes by P(AM-DMC).

## 4. Conclusions

The cationic flocculant P(AM-DMC) effectively decolorizes the water soluble anionic dyes in our tests. Cationicity is the key factor in influencing the decolorization performance, but intrinsic viscosity  $[\eta]$  has little influence on the DE of dyes.

Chemical interaction is observed between sulfonic groups of dyes and quaternary ammoniums of flocculant, and both electrostatic interaction and hydrophobic interaction exist in the binding processes. The electrostatic interaction is related to the number of sulfonic groups in dye molecule, the hydrophobic interaction between dye and polycation become stronger when the volume of aromatic rings of dye increased, and the cooperative interaction also contributes to the binding mechanism.

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