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Dyeing Properties and Colour Characteristics of a Novel Fluorescent Dye Applied to Acrylic Fabric

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Abstract

In this paper, hemicyanine fluorescent dye, namely, *trans*-4-[*p*-(*N,N*-diethylamino)-styryl]-*N*-methyl pyridinium bromide (DEASPBr), was synthesised and applied to the dyeing of acrylic fabric using the traditional cationic dyeing procedure. The absorption spectra of the novel dye were studied under various pHs, and the dyeing properties, fluorescent reflectance, and colorimetric properties were also explored. The results showed that the adsorption mechanism of DEASPBr on acrylic fibre was in good accordance with the Langmuir type, and the dye had an obvious fluorescent effect. In addition, according to the EN-471 standard, the dye could meet the requirements of the fluorescent orange dye for high visibility warning clothing in terms of chromaticity co-ordinates and luminance factors when its concentration was limited in the appropriate range.

Key words: hemicyanine dye, cationic fluorescent dye, acrylic fibre, dyeing, adsorption.

polyacrylonitrile, modacrylic, polyamide and m-aramid fibres have important applications in these textiles. However, acrylic fabric plays an important role in the manufacture of such textiles due to their desirable properties, such as a soft wool-like texture, good elasticity, and high resistance to outdoor exposure.

Fluorescent dyes used in textiles mainly include derivatives of coumarin [3, 4], 1,8-naphthalimide [2], pyrene [5], anthraquinone [6], hemicyanine-azo [7], etc. Hemicyanine dyes, as a type of important cyanine dye, have been largely synthesised and studied, most of the researches of which were focused on optical and medical areas [8], but few reports have been done in fabric application. Our previously published work concerned the dyeing properties of four synthesised hemicyanine fluorescent dyes containing dihydroxyethyl groups for acrylic and silk fabrics [12 - 14].

In this work, one novel stilbene-type hemicyanine dye without dihydroxyethyl groups: *trans*-4-[*p*-(*N,N*-diethylamino)-styryl]-*N*-methyl pyridinium bromide (DEASPBr) was the main focus, and used as cationic fluorescent dye to prepare fluorescent acrylic fabric. The effects of pHs on the absorption spectra of the dye in water were discussed, and the dyeing properties, colour character-

istics and fluorescent reflectance of dyed acrylic fabric were also investigated. In addition, according to the EN-471 standard (2003), the chromaticity of the dyed acrylic fabric was calculated to evaluate whether the dye could meet the requirements of fluorescent dye for high visibility warning clothing.

Experimental

Materials

Acrylic fabric for colour fastness tests (GB/T 7568.5-2002, equivalent to ISO 105-F05: 2001) was obtained from the Shanghai Textile Industry Institute of Technical Supervision, China and used for the dyeing experiments. The hemicyanine dye DEASPBr was synthesised following reference [15 - 17], the molecule structure of which is shown in **Figure 1**. Sodium sulfate, acetic acid, orthophosphoric acid, boric acid and sodium hydroxide were the laboratory reagent grade chemicals used, and purchased from Sinopharm Chemical Reagent Shanghai Co. Ltd., China. Levelling Agent O (a nonionic surfactant, polyoxyethylene alkyl ether) was provided by Jiangsu Hai'an Petrochemical Plant, China and used as received.

Dyeing methods

Dyeing was carried out in a XW-ZDR-25 oscillating sample dyeing machine (Ji-

Introduction

In accordance with the generally accepted definition, fluorescent dyes are considered to be those which absorb and emit radiation in the visible spectral range [1]. Nowadays fluorescent dyes are widely applied in various fields. One of the major application fields where fluorescent dyes have long been used is for the dyeing of textiles. The use of fluorescent dyes causes a significant increase in colour brightness, saturation and visibility, which makes the dyed textiles more easily perceptible. This intensified perceptibility of textiles dyed with fluorescent dyes is an advantage in manufacturing sports clothes and apparel for fire fighters and policemen [1]. In addition, the continuous development of automobile traffic and safety regulations connected to it has resulted in an increasing demand for high-visibility textiles [2]. Polyester,

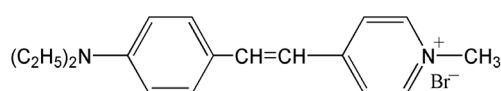


Figure 1. Chemical structure of DEASPBr.

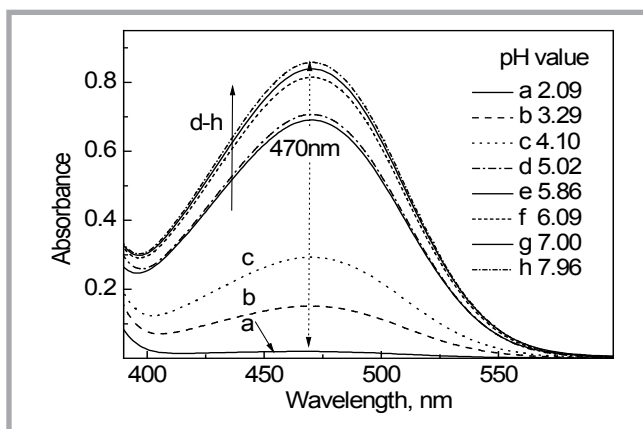


Figure 2. pH-dependent changes in absorption spectra of DEASPBr (dye concentration: 5.5×10^{-5} mol/l).

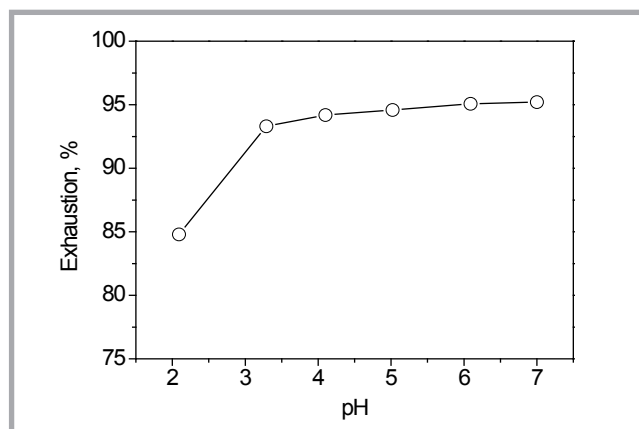


Figure 3. Effect of pH on dye exhaustion (dye concentration: 1% owf).

angsu Jingjiang Xingwang Dyeing and Finishing Machinery Factory, China). All of the dye solutions were prepared with the cationic dye, sodium sulfate (4 g/l) and Levelling Agent O (0.5g/l), and the pH of the dyebath was maintained by a Britton-Robinson buffer solution ($\text{H}_3\text{PO}_4\text{-HOAc-H}_3\text{BO}_3/\text{NaOH}$). The liquor-to-goods ratio was kept at 100:1. The dyeing of the acrylic fabric followed the traditional cationic dyeing process. After immersing acrylic fabric in the dye solutions at 40 °C, the temperature was increased to 80 °C at the rate of 2 °C/min then raised to 95 °C at 1 °C/min, with a holding time of 60 min, and finally cooled to 70 °C at 2 °C/min. At the end of dyeing, the dyed acrylic fabric was rinsed thoroughly in distilled water and allowed to dry in the open air.

To assess the effect of pH on dye exhaustion, the samples were dyed with solutions of 1% owf dye over a range of pH values between 2.09 and 7.00. The adsorption isotherms of dye for acrylic fabric were determined by using a series of dye solutions of various concentrations (0.1 - 3.5% owf) at pH 5.02 and 7.00. For the building-up study, up to 3.5% owf initial dye concentrations were used, and the pH of the dyebath was adjusted to 5.02.

Absorption spectra of dye solutions

In order to study the absorption spectra of the novel hemicyanine dye under various pHs, the pH values (2.09 - 7.96) of the dye solutions (5.5×10^{-5} mol/l) were adjusted with Britton-Robinson buffers. Then the solutions were measured by a UV-1800 UV-vis spectrophotometer (Shimadzu, Japan).

Measurements

Dye uptake was determined by measuring the absorbance of diluted dyebath samples at the maximum absorption wavelength of the dye. A UV-vis spectrophotometer was used to measure the absorbance of dye solutions before and after exhaustion. The percentage of exhaustion (%E) was calculated using Equation 1:

$$\%E = 100 \times \frac{A_0 - A_i}{A_0} \quad (1)$$

where A_0 and A_i are the absorbance of dye solutions before and after exhaustion, respectively.

The apparent colour depth (K/S), chromaticity co-ordinates (x, y), colour co-ordinates (L^*, a^*, b^*), tristimulus values (X, Y, Z) and reflectance spectra (R) of the dyed acrylic fabric were measured on an UltraScan PRO reflectance spectrophotometer (HunterLab, USA), which uses diffuse/8° geometry with an integrating sphere. All measurements were performed under the conditions of a D65 illuminant and 10° observer.

The wash fastness of the dyed fabric was determined by a WashTec-P fastness tester (Roaches International, England) using the standard test method ISO 105-C06. The rubbing fastness was measured on a Model 670 crockmaster (James H. Heal, England) according to ISO 105-X12. The colour fastness to light was measured using an Atlas Xenotest Alpha (SDL Atlas, USA) light fastness tester according to ISO 105-B02.

Results and discussion

Absorption spectra of the dye at different pHs

Previous researches reported that the molecules of hemicyanine dyes may ex-

ist in two forms of monocation and dication in solutions, with the dication form predominating at low pH, which could be reflected in their different absorption spectra at various pHs [12, 18 - 20]. Acrylic fabrics are usually dyed with cationic dyes under weakly acidic conditions. Taking the application pH values of the novel dye into consideration, its absorption characteristics at various pHs were discussed.

The results in **Figure 2** showed that the absorption spectra of DEASPBr changed a little when the pH values were between 5.02 and 7.96, but changed a lot when $\text{pH} \leq 4.10$, and the absorbance became almost zero when $\text{pH} \leq 2.09$.

These phenomena could be explained in terms of the protonation with respect to the formation of a cationic amino group at lower pH [12, 18 - 20]. It is speculated that the molecule of the hemicyanine dye could change from a monocation form to a dication form by protonation as the pH of the application decreased, which may weaken the ability of the electron donor and result in a decrease in the capability of electron transfer. Thus there was no surprise to see the absorbance at the maximum absorption wavelength in the visible spectral range of the dye decrease with a decreasing pH.

Effect of pH on dye exhaustion

Taking the important effects of pH on the existing form of the novel dye into consideration, it is interesting to find how the pH affects dye exhaustion. **Figure 3** shows the influence of dyebath pH on dye exhaustion. The exhaustion seemed to be slightly low at pH 2.09, and remained almost constant over the pH range of 3.29 - 7.00. From the depend-

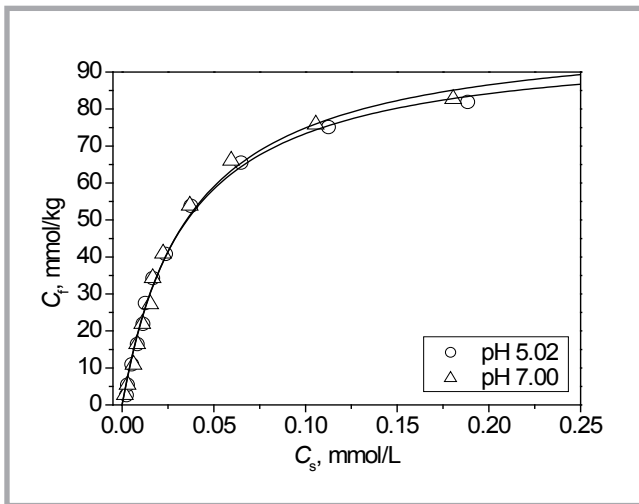


Figure 4. Adsorption isotherms of DEASPBr at two pHs.

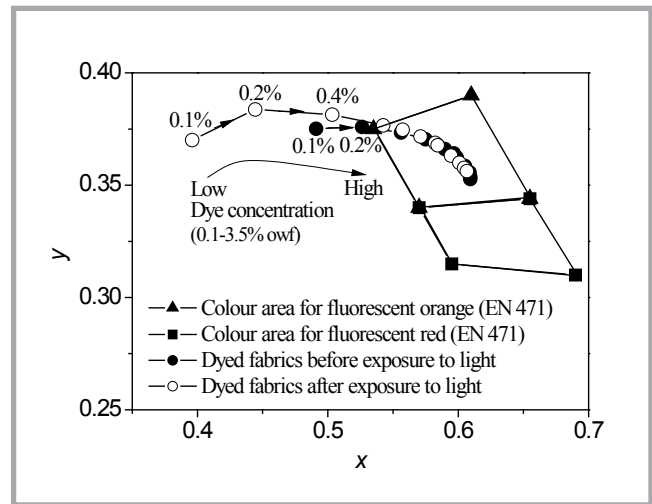


Figure 5. Actual compliance of dyed acrylic fabrics with the EN 471 standard before and after exposure to a xenon lamp.

ence of the absorption spectra and uptake of DEASPBr on pH, it is speculated that both the monocation and dication of the dye could be adsorbed by acrylic fibres. After the dication of the dye diffuse into the interior of fibres, it might transform into a monocation form possibly due to the non-acidic microenvironment of the fibre interior phase. Taking the exhaustion and stability of DEASPBr and the stability of acrylic fibres into consideration, the pH of the dye bath had better be fixed at 5 or so.

Adsorption isotherms

The adsorption of conventional cationic dyes on acrylic fibres occurs by the Langmuir mechanism. In order to deter-

mine the mechanism of the adsorption of DEASPBr by acrylic fibres, the adsorption isotherms of the dye were studied and are demonstrated in Figure 4. It is presumed that the adsorption of the dye could be depicted using the Langmuir model as follows:

$$C_f = \frac{SK_L C_s}{1 + K_L C_s} \quad (2)$$

where C_f and C_s are the concentrations of the dye on fibres and in the solution at equilibrium, respectively; S is the saturation concentration of the dye on acrylic fibres by Langmuir; K_L is the Langmuir affinity constant.

The isotherms were fitted using the non-linear least-squares fitting procedure,

and the parameters obtained are summarised in Table 1. Correlation coefficients (R^2) very close to 1 indicated that the adsorption of the dye at two pHs was in accordance with the Langmuir mechanism. Also the adsorption saturation and affinity constant were nearly the same at two pHs.

Building-up properties of the dye and colour characteristics of the dyed fabrics

The building-up property of cationic dye is important for the dyeing of dark shades. The maximum dye adsorption is mainly restricted by the anionic dyeing sites in acrylic fibres, while the apparent colour depth is dependent on the quantity of dye adsorption and the extent of dye diffusion within the fibre interior. Table 2 shows that the quantity of dye adsorption and the apparent colour depth of the dyed fabrics increased as the initial dye concentration increased, indicating DEASPBr possessed good building-up properties.

Table 1. Langmuir adsorption parameters and correlation coefficients of the simulation.

pH	K_L , l/mmol	S , mmol/kg	R^2
5.02	28.94	98.70	0.99361
7.00	27.20	102.43	0.99167

Table 2. Building-up properties of the dye and colour characteristics of dyed fabrics before exposure to a xenon lamp.

Dye amount, % owf	C_f , mmol/kg	K/S	L^*	a^*	b^*	C^*	h	R , %	x	y	β
0.10	2.64	2.44	85.03	49.43	53.53	72.87	47.28	144.8	0.49	0.38	0.66
0.20	5.47	4.84	81.30	58.15	63.13	85.84	47.35	151.5	0.53	0.38	0.59
0.40	10.99	9.81	75.70	64.17	69.57	94.65	47.31	146.5	0.56	0.37	0.49
0.60	16.45	15.97	71.05	66.97	72.59	98.77	47.31	139.0	0.57	0.37	0.42
0.80	21.90	20.76	67.60	67.50	72.76	99.25	47.15	130.4	0.58	0.37	0.37
1.00	27.54	23.70	65.55	67.91	72.76	99.53	46.98	125.9	0.59	0.37	0.35
1.25	34.32	29.18	62.35	67.53	72.26	98.90	46.94	116.8	0.60	0.36	0.31
1.50	40.82	29.87	60.47	67.12	70.66	97.46	46.48	111.6	0.60	0.36	0.29
2.00	53.84	33.93	56.78	66.49	68.31	95.33	45.78	102.9	0.61	0.36	0.25
2.50	65.50	38.38	52.63	64.34	64.66	91.22	45.14	90.7	0.61	0.36	0.21
3.00	75.14	38.57	50.87	63.45	62.21	88.86	44.43	87.0	0.61	0.35	0.19
3.50	81.93	41.42	47.74	60.79	58.81	84.59	44.05	76.4	0.61	0.35	0.17

Usually the maximum reflectance value of fabrics dyed with fluorescent dyes is higher than 100%. As shown in Table 2, the maximum reflectance of the acrylic fabrics dyed with DEASPBr was above 100% in a dye concentration range of 0.1 - 2.0% owf, where the reflectance increased with the dye concentration in certain concentration ranges, but decreased due to the fluorescence quenching effect when the concentration exceeded some critical value.

In order to determine the possibility of applying the novel hemicyanine dye to

Table 3. Colour characteristics of dyed fabrics after exposure to a xenon lamp.

Dye amount, % owf	K/S	L*	a*	b*	C*	h	R, %	x	y	β
0.10	0.45	89.05	18.56	29.29	34.67	57.66	105.2	0.40	0.37	0.74
0.20	1.22	87.54	30.76	45.10	54.59	55.71	120.5	0.44	0.38	0.71
0.40	3.90	79.50	47.95	56.77	74.31	49.82	123.4	0.50	0.38	0.56
0.60	8.06	74.47	58.30	64.74	87.12	48.00	128.8	0.54	0.38	0.47
0.80	11.61	70.48	60.36	66.63	89.91	47.83	121.4	0.56	0.37	0.41
1.00	15.65	68.21	63.36	69.16	93.80	47.51	122.0	0.57	0.37	0.38
1.25	21.58	64.34	64.13	69.50	94.56	47.31	113.5	0.58	0.37	0.33
1.50	22.08	63.12	63.99	68.79	93.96	47.07	110.3	0.58	0.37	0.32
2.00	27.83	58.93	64.46	67.56	93.38	46.34	101.7	0.59	0.36	0.27
2.50	32.27	55.98	64.36	66.27	92.38	45.84	95.7	0.60	0.36	0.24
3.00	36.60	53.26	63.43	64.26	90.29	45.38	88.9	0.60	0.36	0.21
3.50	36.35	51.08	62.31	62.47	88.24	45.08	82.6	0.61	0.36	0.19

Table 4. Fastness properties of DEASPBr (dye concentration: 0.6% owf).

Colour change	Washing fastness						Rubbing fastness		Light fastness
	Staining						Dry	Wet	
	Wool	Acrylic	Polyester	Polyamide 66	Cotton	Acetate			
5	5	5	5	5	5	5	5	4 - 5	3 - 4

high-visibility textiles, the dyed fabrics before and after exposure to a xenon lamp were assessed in terms of chromaticity co-ordinates (x , y) and luminance factors (β). According to the requirements of the EN-471 standard, textiles designed for manufacturing high visibility garments must conform to certain values specified for a particular colour. For orange-red colours, the chromaticity co-ordinates x and y should fall within a specified area (Figure 5), and the luminance factor β should be equal to or greater than 0.40. The luminance factor β is measured as Y/Y_0 , where $Y_0 = 100$ is the three-chromatic co-ordinate for a perfect reflecting diffuser. The results of these measurements are given in Tables 2 and 3, and also presented in Figure 5.

From the chromaticity co-ordinates (x , y) and colour co-ordinates (a^* , b^* and h^*) shown in Tables 2 & 3, and Figure 5, it can be seen that the colour parameters of acrylic fabrics dyed with DEASPBr before and after exposure to a xenon lamp were in the yellow and red section when the initial dye concentration exceeded 0.6% owf, indicating the fabrics displayed a reddish orange colour. The luminance factor β decreased with an increase in the concentration of dyes in the fibre. When the dye concentration was 0.6% owf, both the luminance factor and chromaticity co-ordinate of the dyed acrylic fabric before and after light exposure could meet the requirements of fluo-

rescent orange of the EN-471 standard. Thus the acrylic fabrics dyed with the novel dye at a concentration of 0.6% owf could be used in high-visibility warning clothing in terms of chromaticity co-ordinates and luminance factors.

To the best of our knowledge, there is a lack of orange species among commercial, fluorescent cationic dyes in terms of colour hues. Thus the application of the novel orange dye can increase the colour species of cationic fluorescent dyes.

Colour fastness of dyeings

Colour fastness was tested according to standard methods, the results of which are given in Table 4. As shown in Table 4, the light fastness arrived up to 3 - 4, and the washing and rubbing fastness were all about grade 5, hence the acrylic fabrics dyed with the novel fluorescent dye had fairly good colour fastness.

Conclusions

Considering the spectral and fastness data as well as chromaticity co-ordinates and luminance factors, the novel hemicyanine dye DEASPBr seems to be the most promising product for the fluorescent orange coloration of high-visibility warning acrylic fabrics when its concentration was limited in the appropriate range. Its uptake by acrylic fibres fol-

lowed the Langmuir mechanism. The pH of the dyebath should be fixed at 5 or so.

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