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Effect of pH on the Fading Behavior of Vinylsulfonyl Azo Dyes on Cellulose in Aqueous Solutions

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ABSTRACT

The effects of pH on the fading of three vinylsulfonyl azo dyes on cellulose immersed in aerobic and anaerobic aqueous solutions were investigated in the pH range between 2·5 and 9. Under anaerobic conditions, the rates of reductive fading for C.I. Reactive Red 22 and Black 5 increased with a decrease in pH only in the acid region, whereas those for a copper-complex azo dye (Blue-Cu) were almost negligible over all the pH range examined. The rates of fading for Black 5 and Blue-Cu in aerobic water decreased with increasing pH in the acid region and increased in the alkaline region. Black 5 on cellulose underwent simultaneous oxidative and reductive fading on exposure in aerated water, although greater oxidative fading was observed at pH ≥ 8. Vinylsulfonyl azo dyes on cellulose have a tendency to show increased fading at both extreme pHs on exposure under wet conditions.

1 INTRODUCTION

Oxidative fading of azo dyes occurs via a singlet-oxygen mechanism from their hydrazone form,[1–4] whereas reductive fading occurs via a hydrogen-abstraction mechanism from the azo form.[5] Azo-hydrazone tautomerism depends not only on the chemical structure[6–13] but also on environmental conditions, such as solvent,[6,7] polymer substrate,[6] pH of the aqueous solution,[14,15] and temperature.[7] The fading behaviour of azo dyes on cellulose has been shown to be dependent on environmental conditions such as the concentration of oxygen,[16] the substrate from which the dyes abstract hydrogen,[17] and moisture.[18]

In the azo-hydrazone tautomerism, azo tautomers predominate at higher pH,[14,15] and hydrazone tautomers at lower pH, depending on the environmental conditions. Since many azo dyes undergo oxidative and/or reductive fading under neutral conditions, commercial dyes usually exist in a mixture of the azo and hydrazone tautomers, [17,19] although azo tautomers predominate in some dyes developed recently. C.I. Reactive Red 22 and Black 5 on cellophane immersed in aerobic water (pH 6·0) underwent oxidative and/or reductive fading irrespective of the absence of substrate.[18]

In Japan, testing methods for the color-fastness to light and perspiration examine the color changes of the exposure of dyed fabrics after immersing them in artificial perspiration at pH 5·5 and 8·0.[20] No essential cause of the pH effect on the fading of dyes, other than of metal-complex azo dyes, in this testing method has so far been elucidated. Color variations are also observed on the immersion of fabrics dyed with copper-complex azo dyes in aqueous histidine and become greater with an increase in the pH of the histidine solution.[21] It has been considered that the increased fading by alkaline artificial perspiration compared with that in acidic conditions may be mainly due to the higher co-ordination of histidine to copper-complex dyes.[22]

Asquith and Ingham[23] found no pH effect on the fading of C.I. Acid Violet 4 in aqueous solutions. However, the rate of production of singlet oxygen by Methylene Blue on illumination has been reported to increase fivefold in going from pH 5 to 9.[24] The kinetics and mechanisms of photosensitized oxidations of α-amino acids in solution depend upon the amino acid, the sensitizer, the solvent, the relative concentration of the reactants, the type of buffer, and the pH. [25,26] Extensive investigations on the pH-dependence of the photo-oxidation of α-amino acids have been carried out by use of various dye sensitizers.[27]

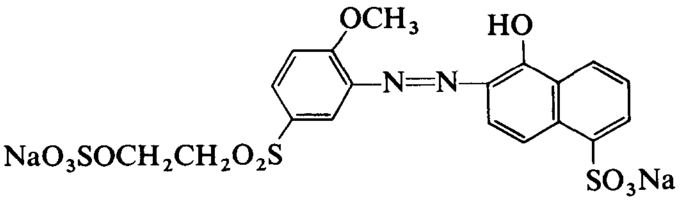
In the present study, the fading behavior of some vinylsulfonyl (VS) azo dyes on cellophane immersed in deaerated and aerated aqueous solutions at different pH values is investigated. The fading mechanism at various pHs is examined by using spectral analysis.

2 EXPERIMENTAL

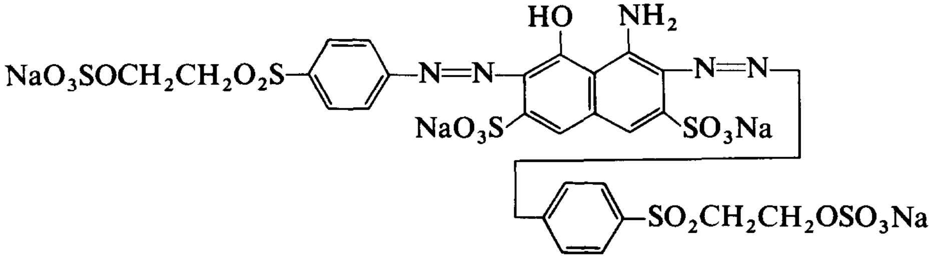
2.1 Dyes used

C.I. Reactive Red 22 and Black 5 were supplied by Sumitomo Chemical Co. Ltd and a copper-complex azo dye by Hoechst Mitsubishi Kasei Co. Ltd. The dyeing methods for cellophane were the same as those used previously.[28] The chemical structures of the dyes used are as follows:

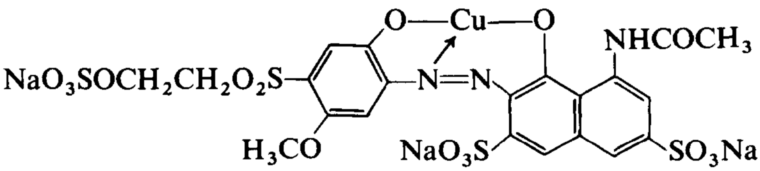
(1) C.I. Reactive Red 22; C.I. 14824 (Red 22)



(2) C.I. Reactive Black 5; C.I. 20505 (Black 5)



(3) A copper-complex azo dye (Blue-Cu)



2.2 Exposure

The method of exposure and the apparatus were the same as previously described.[29] A sheet of dyed film was set in a glass cell filled with an aqueous solution at a given pH and was exposed to a carbon arc in a fadeometer. Phosphate buffer solutions (0·001M) of pH 3–9 were prepared with sodium dihydrogen phosphate, disodium hydrogen phosphate, trisodium phosphate, and phosphoric acid, and aqueous phosphoric acid (0·004M) was used at pH 2·5. The chemicals were of reagent grade and were used as received. A glass plate was used at the rear of the sample and set in a glass cell during exposure to prevent the penetration of trace oxygen.[17] After exposure, all the films were thoroughly washed in aqueous dimethylformamide (10 vol. %) at 60°C and then in boiling water to remove photodecomposed fragments that were not bound by cellulose completely.

2.3 Spectral analysis of photodecomposition products

The absorption spectra of decomposition products were obtained by subtracting the corresponding spectrum of the original dye from the spectrum of the dyed film exposed in an aqueous solution.[30]

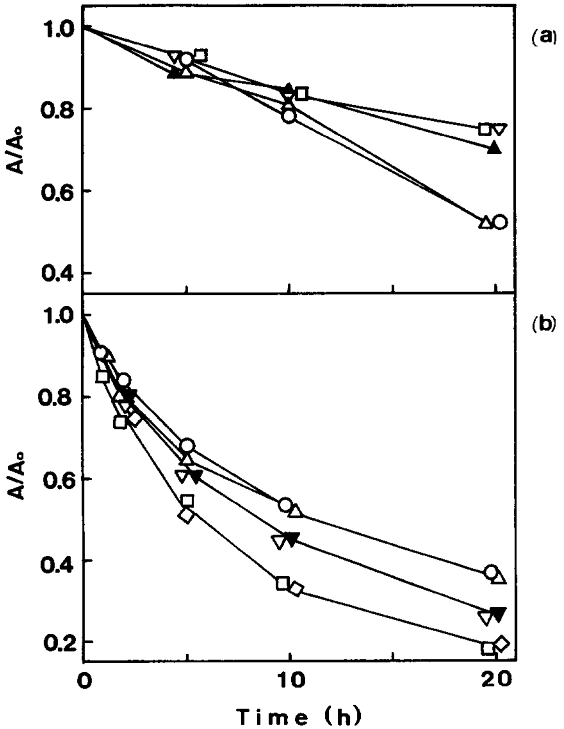


Fig. 1. Relative fading of C.I. Reactive Red 22 (original dye concentration = 2·02 × 10^{-2} mol kg^{-1}) on cellophane exposed in aqueous solution at pH 3·03 (○), 4·03 (△), 5·02 (▲), 6·01 (▽), 7·04 (▼), 7·99 (◇), and 9·01 (□) under (a) anaerobic and (b) aerobic conditions.

3 RESULTS AND DISCUSSION

3.1 Effect of pH on the fading of Red 22

3.1.1 Fading under anaerobic conditions

On exposing the dyed cellophane immersed in anaerobic water (pH 6·0), Red 22 underwent slow reductive fading, whereas in aerobic water it underwent oxidative fading.[30]

The fading behavior of Red 22 on cellulose immersed in 0·001M phosphate buffer under anaerobic conditions is shown in Fig. 1(a). The absorption spectra of the photodecomposition products showed only the formation of reduction products.[30] The amounts of the photoreduction products were in accord with those of fading, within experimental error.

The rates of reductive fading were constant at pH ≥ 6 and also at pH ≤ 4, but the former rates were lower than the latter, as shown in Fig. 2. The rates at pH 5 were intermediate between these, a transition region in the rate of reductive fading. According to Yamamoto *et al.*,[13] azo groups in the *o*-position to hydroxyl groups in water-soluble azo dyes exist in the hydrazone form in dimethylsulfoxide. To judge from the pH-dependence of the reductive fading, this transition behavior around pH 5 may be the reverse to that of the azo–hydrazone tautomerism. It may then be attributed to the transition region of the reduction potential of the excited states for Red 22.

3.1.2 Fading under aerobic conditions

As shown in Fig. 1(b), the rate of fading for Red 22 on exposure in aerated water increased with increase in pH (cf. Fig. 2). The absorption spectra of the photodecomposition products implied that only photo-oxidation occurs on exposure in aerated water.[30] The amounts of the oxidation products also coincided with those of fading, within experimental errors.

The increase in the oxidative fading with pH below pH 6 may be due to an increase in the rate of production of singlet oxygen with pH.[24] There is little doubt that, with many photosensitizers, histidine is photo-oxidized via a singlet-oxygen mechanism, especially above pH 6.[27] Thus, the singlet-oxygen mechanism is more predominant in the alkaline region than in the acid region. The pH-dependence of the photo-oxidation for Red 22 is similar to the photosensitized oxidation for amino acids,[24–27] which increase with increase in pH.

In order to compare the pH-dependence of the reductive fading under anaerobic conditions with that of the oxidative fading under aerobic con-

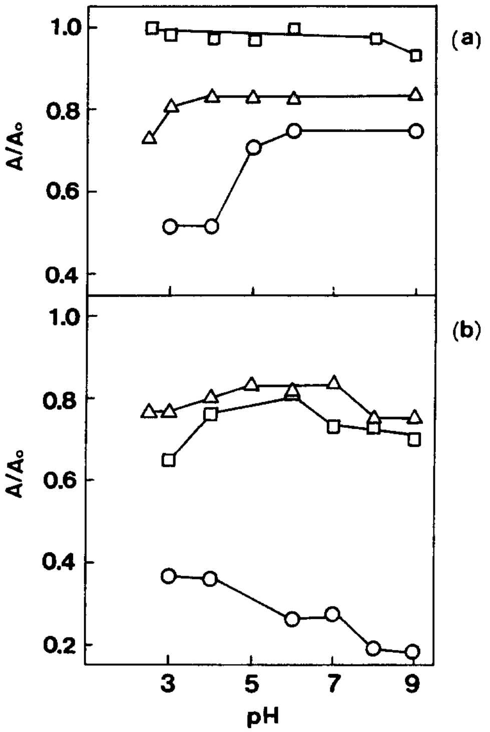


Fig. 2. Effects of pH on fading for C.I. Reactive Red 22 (○), Black 5 (Δ), and Blue-Cu (□) on cellophane on exposure for 20 h in (a) anaerobic and (b) aerobic aqueous solutions of phosphate (0·001M, pH 3–9) and phosphoric acid (0·004M, pH 2·46) at 50°C (cf. Figs 1, 3, and 4).

ditions, the relative fading after exposure for 20 h was plotted against the pH (Fig. 2). With increasing pH, the oxidative fading tended to increase, whereas the reductive fading tended to decrease, except at pH ≤ 4. To judge from the pH-dependence of fading for Red 22, azo-hydrazone tautomerism seems to play a minor role in the pH effect. In the case of photo-oxidation, the increasing rate of singlet-oxygen generation may contribute to the increase in the oxidative fading with an increase in pH.[24–26]

3.2 pH-dependence of the fading of Black 5

3.2.1 Fading under anaerobic conditions

The fading of Black 5 on cellulose under anaerobic conditions showed little pH-dependence, except for fading at low pH (Fig. 2. (a)). In order to confirm this, Black 5 was exposed in deaerated aqueous phosphoric acid (0·004M, pH 2·46) and underwent increased fading. Hydrogen ions

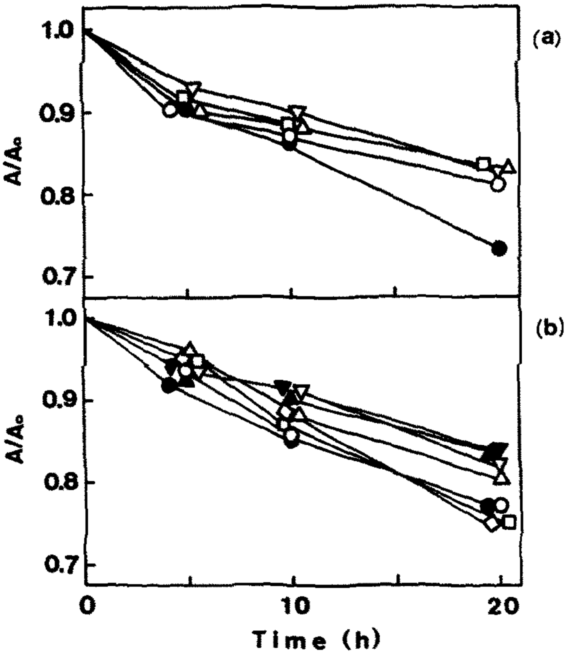


Fig. 3. Relative fading of C.I. Reactive Black 5 (original dye concentration = 5·03 × 10^{-3} mol kg^{-1}) on cellophane exposed in aqueous solutions at pH 2·46 (●), 3·03 (○), 4·03 (△), 5·02 (▲), 6·01 (▽), 7·04 (▼), 7·99 (◇), and 9·01 (□) under (a) anaerobic and (b) aerobic conditions.

may decrease the reduction potential of azo groups in the excited state of dyes. This behavior was observed at pH ≤ 5 in the case of Red 22.

The absorption spectra of the photodecomposition products, which were obtained by spectral analysis, showed that the amino end-products as well as some monoazo intermediates were formed by exposure of Black 5 under anaerobic conditions.[30] The quantitative relation between the fading and the formation of reduction products could not be determined, since both the reactive groups of Black 5 were not always bound with cellulose. Complete reduction of the exposed and unexposed films dyed with Black 5 in aqueous sodium dithionite (0·1M, 70°C) showed that the same amounts of reduction products remained on the cellulose, i.e. only photoreduction occurs on exposure under anaerobic conditions.

3.2.2 *Fading under aerobic conditions*

The rates of fading for Black 5 in aerated water decreased with increase in pH in the acid region and then increased significantly in the alkaline region. The differences in the rates of fading between aerobic and anaerobic conditions were larger at pH 8 and 9 than at pH ≤ 7, which implied greater

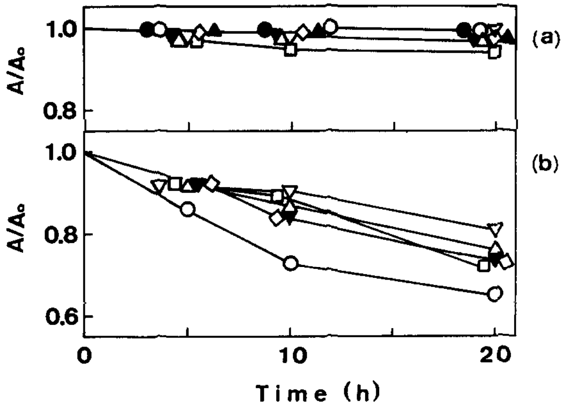


Fig. 4. Relative fading of Blue-Cu (original dye concentration = 1·20 × 10^{-2} mol kg^{-1}) on cellophane exposed in aqueous solutions at pH 2·46 (●), 3·03 (○), 4·03 (Δ), 5·02 (▲), 6·01 (∇), 7·04 (▼), 7·99 (◇), and 9·01 (□) under (a) anaerobic and (b) aerobic conditions.

oxidative fading in the alkaline region. From spectral analysis of the photodecomposition products on cellulose after the exposure under aerobic conditions, it was shown that, in addition to oxidative fading, reductive fading also occurred over the pH region examined. Besides the reductive end-products, some reddish monoazo intermediates were observed, as in case of the exposure in aerobic solutions of substrates such as lactic acid and DL-mandelic acid.[30] Since both the reactive groups of Black 5 were not always bound with cellulose, the amounts of photo-oxidation and photoreduction could not be precisely determined. However, the complete thermal reduction of the dyed film exposed under aerobic conditions with sodium dithionite showed smaller amounts of reduction products at pH 8 and 9 than at pH ≤ 7, which implied greater oxidative fading under alkaline conditions.

In order to examine the fading behavior at low pH, the film dyed with Black 5 was also exposed in aerobic water at pH 2·5. The rate of fading at pH 2·5 was a little greater than that in anaerobic water at the same pH. Spectral analysis of the photodecomposition products showed that both oxidative and reductive fading occurred.

It has been reported[12,13] that azo groups ortho to the amino groups of H-acid are in the azo configuration, whereas those ortho to the hydroxyl groups are in the hydrazone form. The effect of tautomerism on the pH-dependence of fading could not, however, be clarified.

Under mild conditions, the effects of ionic strength and the type of buffer on the fading of Red 22 and Black 5 on cellulose immersed in aerated aqueous buffer were also observed. They were smaller in phosphate buffer than in borate buffer (0·01M) at pH 9, where very large fading of these dyes occurred. The influence of the nature of the buffer has been reported in the case of photosensitized oxidation of α-amino acids,[25,26] but this behavior still remains to be elucidated.

3.3 Effect of pH on the fading of Blue-Cu

As shown in Figs 2 and 4, Blue-Cu showed little fading on exposure under anaerobic conditions, except for the case of pH 9. The absorption spectra of the decomposition products at pH 9 showed the formation of reduction products. Some vinylsulfonyl[17] and monochlorotriazinyl[31] reactive dyes on cellulose showed similar behavior.

Blue-Cu cellophane immersed in aerated water showed the same pH dependence on the rate of fading as that of Black 5 (cf. Fig. 2). Thus, the rates of fading decreased with increase in pH at pH < 6, and increased at pH > 6. The absorption spectra of the exposed films showed some evidence indicating oxidative, but no reductive decomposition of the azo groups. Since no absorption spectrum of the decomposition products was observed, it is presumed, as has been previously reported[18], that the oxidation products formed on cellulose were split off in the subsequent photoreduction.

4 SUMMARY

The pH-dependence of the fading of three vinylsulfonyl reactive dyes, C.I. Reactive Red 22, Black 5, and Blue-Cu, on cellulose immersed in an aqueous solution was examined under anaerobic and aerobic conditions. With an increase in pH in the acid region, the rates of reductive fading for Red 22 and Black 5 under anaerobic conditions and those of oxidative fading for Blue-Cu under aerobic ones decreased, whereas those of oxidative fading for Red 22 increased under aerobic conditions.

The rates of reductive fading for the three dyes under anaerobic conditions in the alkaline region showed little pH-dependence. The rates of oxidative fading under aerobic conditions increased with increasing pH in the alkaline region.

For the vinylsulfonyl dyes examined in this study, no evidence of correlation of pH-dependence was found between the rates of fading and the azo-hydrazone tautomerism.

In general, some vinylsulfonyl azo dyes on cellulose on exposure under wet conditions have a tendency to show increased fading at both extreme pHs.

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