Influence of Polyacrylamide on the Oxidative Decomposition of Sodium Dithionite: Implications for Vat Dyeing Processes

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SYNOPSIS

A statistical analysis was made of the halftimes of oxidative decomposition of sodium dithionite at 25°C in alkaline aqueous solutions, having geometrically spaced specific surfaces and concentrations of polyacrylamide. The analysis reveals a strong relationship between solution-specific surface and resulting halftime, with halftime decreasing as specific surface increases; however, only the highest concentration of polyacrylamide, with a correspondingly high solution viscosity, is revealed to have a consistently significant effect on the rate of oxidative decomposition of dithionite. No significant effect on dithionite decomposition is observed for polyacrylamide concentrations that conceivably would be used in commercial vat dyeing processes. The findings suggest that the beneficial effect of high molecular weight polymers such as polyacrylamide in commercial vat dyeing is due solely to the function of the polymer to decrease the specific surface of the dithionite solution on the fabric, leading to decreased decomposition rates. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

As long ago as 1965, Ulrich and Schraub found that the substitution of a very high molecular weight polyacrylamide thickening agent for sodium alginate in the padbath, i.e., in the vessel containing the dyes and chemicals with which the fabric is impregnated, resulted in increased color depth in continuous thermal fixation dyeing of polyester fiber with disperse dyes.[1] Disperse dyes are sparingly water-soluble dyes that may be applied in the form of a vapor to hydrophobic fibers. Analysis has revealed two fundamental causes for the observed color depth increase.[2] First, polyacrylamide is not an effective antimigrant; its use does not result in control of particulate migration of the disperse dye particles in the capillary spaces of the impregnated fabric during intermediate drying. Dye particles therefore migrate to the fibers in the fabric surface where molecular dye is released as a vapor during heat fixation and is adsorbed by the fiber. Such surface dyeing results in greater color depth for a given amount of fixed dye than would occur if the dye were uniformly dis-

tributed in the cross section of the fabric. Second, polyacrylamide promotes increased pickup of the padbath by the fabric, increasing the amount of dye on the fabric after impregnation and resulting in an additional increase in color depth.

Further use has been made of the ability of high molecular weight polymeric additives to promote increased dyebath pickup or adhesion in discontinuous pad-jig dyeing of cotton fabric with indigoid or anthraquinone *vat* dyes.[3] Pad-jig dyeing essentially consists of first impregnating the fabric with the insoluble vat dye pigment and then drying the impregnated fabric. The fabric is then passed repeatedly through a reducing agent solution of sodium hydroxide and sodium hydrosulfite at a temperature of about 80°C to convert the insoluble pigment to the water-soluble form that diffuses into the cellulosic fiber. Inclusion of the polymeric additive in the solution of reducing agent was shown to decrease dyeing imperfections that were caused by premature oxidation of the reduced, water-soluble form of the vat dye on the fabric. Also, recent data reveal that the use of high molecular weight additives can be useful in continuous pad-steam dyeing with vat dyes.[4] This form of continuous dyeing consists of impregnating a cellulosic fabric or blend with a dis-

persion of vat pigment, drying the fabric, passing the fabric into a "chemical padbath" containing sodium hydroxide–sodium hydrosulfite reducing agent, and then steaming the fabric to bring about reduction of the dye to the soluble form that diffuses into the cellulosic fiber. When high molecular weight polymeric additives are included in the chemical padbath, oxidation of reducing agent on the fabric between the chemical padbath and steamer is minimized, resulting in increased color yield. In each of the two dyeing investigations cited above, the data suggested that the beneficial effect of the polymeric additives was due to nothing more than the function of the additive to reduce the ratio of the reducing solution surface area for a given solution volume (specific surface) picked up by the fabric, resulting in a slower rate of oxidative decomposition of reducing agent. Previous research has shown that the rate of oxidative decomposition of dithionite is strongly dependent on the magnitude of the specific surface of the solution containing the reducing agent.[5,6]

Research Objective

Previous investigations of the effect of high molecular weight polymeric additives in vat dyeing processes have involved the use of auxiliaries having a proprietary chemical nature. In addition, the investigations have not addressed the question of whether or not viscosity influences the apparent diffusion coefficient of the dithionite ion radical. The purpose of the present investigation has been to conduct a statistical analysis of the effect of a chemically well-defined high molecular weight polymer on the half-time of oxidative decomposition of sodium dithionite and to determine whether or not a viscosity effect exists.

EXPERIMENTAL

Materials

Polyacrylamide. Cyanatex 695, a white free-flowing powder, having a mean molecular weight of about 16 million and supplied by American Cyanamid Company.

Sodium Dithionite. Virtex D, a dry particulate powder, having an activity of about 90% and supplied by Hoechst Celanese.

Sodium Hydroxide. Pellet form, supplied by Baker.

Procedure

Ten grams per liter stock solutions of polyacrylamide and 100 g/L stock solutions of sodium hydroxide were prepared for use in making up the various solutions of sodium dithionite. In all cases, 25 g/L sodium dithionite and 50 g/L sodium hydroxide were used, with a control (no polymer) and with geometrically spaced concentrations of polyacrylamide consisting of 0.1, 0.2, 0.4, 0.8, and 1.6 g/L. The reducing agent solutions were prepared at room temperature (25°C) in 2-L beakers by first adding the necessary amount of sodium hydroxide stock solution to about half the final volume; then the necessary amount of polyacrylamide stock solution was added, followed by the addition of sodium dithionite; the solution then was built to final volume and briefly stirred. An amount of each solution then was poured into cylindrical glass vessels to obtain the desired ratio of surface area to solution volume (specific surface, cm^{-1}). The geometrically spaced specific surfaces consisted of 0.08, 0.16, 0.32, 0.64, 1.28, and 2.56 cm^{-1}.

Titration of Sodium Dithionite

A standard titration technique,[7] employing iodine and a starch indicator was used to follow the decomposition of sodium dithionite over time. The procedure was to follow the decomposition of dithionite in each still, unagitated solution over an 8-h period, with titration samples being taken from the bottom of each solution vessel at 30-min intervals.

Determination of Rate Constant

For each concentration of polyacrylamide and specific surface, the rate constant of decomposition of dithionite, k, was determined by regression analysis of $\ln(C)$ versus time in minutes, where $\ln(C)$ is the natural logarithm of the concentration of dithionite at a given time. The rate constant determination was repeated four times for each reducing agent solution. From a knowledge of the rate constant, the halftime of decomposition, $t_{1/2}$, was determined for each case by

$$t_{1/2} = \frac{\ln(2)}{k} \tag{1}$$

Viscosity Measurement

Solution viscosity measurements were made by the use of a Brookfield viscometer on each solution after

8 h at the conclusion of the titration measurements. Measurement of initial viscosity of selected solutions revealed no apparent viscosity drift during the 8-h period at 25°C.

RESULTS AND DISCUSSION

Rate constants and corresponding halftimes were determined at random for the various experimental conditions over a 10-week period. Mean halftimes and coefficients of variation, obtained for different specific surfaces (A/V) and polyacrylamide concentrations (C), are listed in Table I.

Statistical Analysis

The fundamental question to be answered is: Do significant differences exist between the halftimes given in Table I for different concentrations of polyacrylamide at given specific surfaces? In terms of a formal null hypothesis, H_0, the question can be posed for each specific surface by

$$H_0: (t_{1/2})_0 = (t_{1/2})_{.1} = (t_{1/2})_{.2}$$
$$= (t_{1/2})_{.4} = (t_{1/2})_{.8} = (t_{1/2})_{1.6} \quad (2)$$

where the subscript outside the parenthesis indicates the concentration of polymer. The alternate hypothesis, H_a, is simply stated in words for each specific surface as

$$H_a: \text{Not all halftimes are equal} \quad (3)$$

Null hypotheses, such as the one presented here, usually are tested by use of the statistical technique analysis of variance, or ANOVA. However, for ANOVA to be an appropriate test, the elements of the means that one is testing for equality must be normally distributed with equal variances.[8] Since in the present investigation only four replications have been determined for each of the experimental conditions, one cannot be certain that the halftimes determined at each concentration of polyacrylamide for a given specific surface are normally distributed with equal variances. A nonparametric analysis of variance was therefore used, since the assumptions necessary for the use of such a test do not include the prerequisites of normality and equal variances.[9]

Nonparametric ANOVA

The first step in nonparametric ANOVA is to rank the halftimes from the lowest to the highest, with ties being given a mean ranking. By the use of a statistical package such as SAS,[10] analysis of variance is then made on the ranks. In the present study, the null hypothesis was tested at the significance level of 0.05, i.e., if the P value that resulted from

Table I   Mean Halftimes $(t_{1/2})$ of Oxidative Decomposition of Sodium Dithionite and Coefficients of Variation (%CV) as a Function of Specific Surface (A/V) and Polyacrylamide Concentration (C)

A/V	C	$t_{1/2}$	%CV	A/V	C	$t_{1/2}$	%CV
0.08	0.0	1351	2.20	0.64	0.0	0221	2.67
0.08	0.1	1367	1.46	0.64	0.1	0219	2.51
0.08	0.2	1357	2.20	0.64	0.2	0218	2.61
0.08	0.4	1350	1.55	0.64	0.4	0228	2.65
0.08	0.8	1337	3.12	0.64	0.8	0222	2.74
0.08	1.6	1604	2.75	0.64	1.6	0247	2.50
0.16	0.0	0746	1.36	1.28	0.0	0123	1.39
0.16	0.1	0743	1.77	1.28	0.1	0120	0.80
0.16	0.2	0740	3.90	1.28	0.2	0120	4.18
0.16	0.4	0748	2.32	1.28	0.4	0119	1.59
0.16	0.8	0774	2.07	1.28	0.8	0119	3.14
0.16	1.6	0867	1.18	1.28	1.6	0140	2.57
0.32	0.0	0406	2.88	2.56	0.0	0063	1.51
0.32	0.1	0405	1.85	2.56	0.1	0064	1.97
0.32	0.2	0407	4.40	2.56	0.2	0065	2.81
0.32	0.4	0404	3.12	2.56	0.4	0066	1.46
0.32	0.8	0409	2.87	2.56	0.8	0067	2.88
0.32	1.6	0460	2.02	2.56	1.6	0075	1.34

the analysis was less than 0.05, the null hypothesis was rejected and a Duncan Multiple Range Test was performed to determine which concentrations of polyacrylamide viscosity produced significant differences in halftime.

Results of Statistical Analysis

The results of the statistical analysis of the null hypothesis for each specific surface are summarized in Table II.

It is revealed in Table II that the P values obtained from the nonparametric ANOVA for all but one of the specific surfaces is less than 0.05. The null hypothesis that the halftimes of oxidative decomposition are the same for all concentrations of polyacrylamide must be rejected for data obtained at each specific surface—except A/V of 0.32. Duncan's Multiple Range Test conducted at an alpha level of 0.05 reveals the reason for the rejection of the null hypothesis. The halftime obtained for the dithionite solution having the highest concentration of polyacrylamide is slightly, but significantly, higher than that obtained for all other polymer concentrations for the specific surfaces 0.08, 0.16, 0.32, and 2.56. No significant difference in halftime is found for dithionite solutions containing all of the other polyacrylamide concentrations for the specific surfaces 0.08, 0.16, and 0.32. It is an interesting statistical anomaly that Duncan's Multiple Range test reveals a significant difference for the halftime at the highest concentration of polymer at a specific surface of 0.32, but the nonparametric analysis of variance does not quite result in rejection of the null hypothesis at that specific surface. In addition, statistically significant differences were detected at an A/V of 2.56 between the two concentrations 0.0 and 0.1 g/L and that obtained for all other concentrations. Furthermore, because of the variances, no significant difference was detected between the

Table II P **Values Obtained for the Nonparametric ANOVA of the Null Hypothesis for Each Specific Surface**

A/V (cm^{-1})	P Value
0.08	0.0288
0.16	0.0496
0.32	0.0518
0.64	0.0032
1.28	0.0046
2.56	0.0002

halftimes obtained for concentrations 0.0 and 1.6 at an A/V of 1.28 or for the concentrations 0.4 and 1.6 at an A/V of 0.64. Nevertheless, for the overall experimental series, a slightly increased halftime is found to be statistically significant for the highest concentration of polymer. A possible reason for the increased halftime is revealed through analysis of the rate constant of oxidative decomposition of sodium dithionite.

Analysis of Rate Constant, k

According to Fromherz[11]:

> In the case of a large number of heterogeneous chemical reactions, especially in those where extensive boundary surfaces or a large homogeneous or interface reaction velocity exists, the rate of reaction is determined by the rate of transport or diffusion, e.g., from inside the solution, through the boundary layer to the interface.

The rate of oxidative decomposition of sodium hydrosulfite is therefore given by

$$\frac{C_t}{C_0} = \exp\left[\frac{-DAt}{V\delta}\right] \qquad (4)$$

where C_t is the concentration of hydrosulfite at a given time t; C_0 is the initial concentration of reducing agent; D is the diffusion coefficient of the hydrosulfite ion radical (cm^2/unit time); A is the area of the solution exposed to air (cm^2); V is the volume of solution (cm^3), and δ is the thickness of the diffusional boundary layer at the solution–air interface (cm). When the ratio of the diffusion coefficient to the boundary layer thickness is treated as a constant, it is possible to determine by use of regression analysis an apparent rate constant, k, from which the halftime of oxidative decomposition of reducing agent for different solution-specific surfaces, A/V, may be determined. However, even in the absence of knowledge of the size of the boundary layer thickness, it is revealed in Eq. (4) that the magnitude of the diffusion coefficient also has a strong influence on the rate of decomposition of dithionite.

As shown in Figure 1, extremely high viscosities may be obtained with relatively low concentrations of the polyacrylamide polymer used in the present investigation.

Although the maximum concentration of polymer used in the present investigation results in a viscosity of only about 17 cps, it is believed that at this
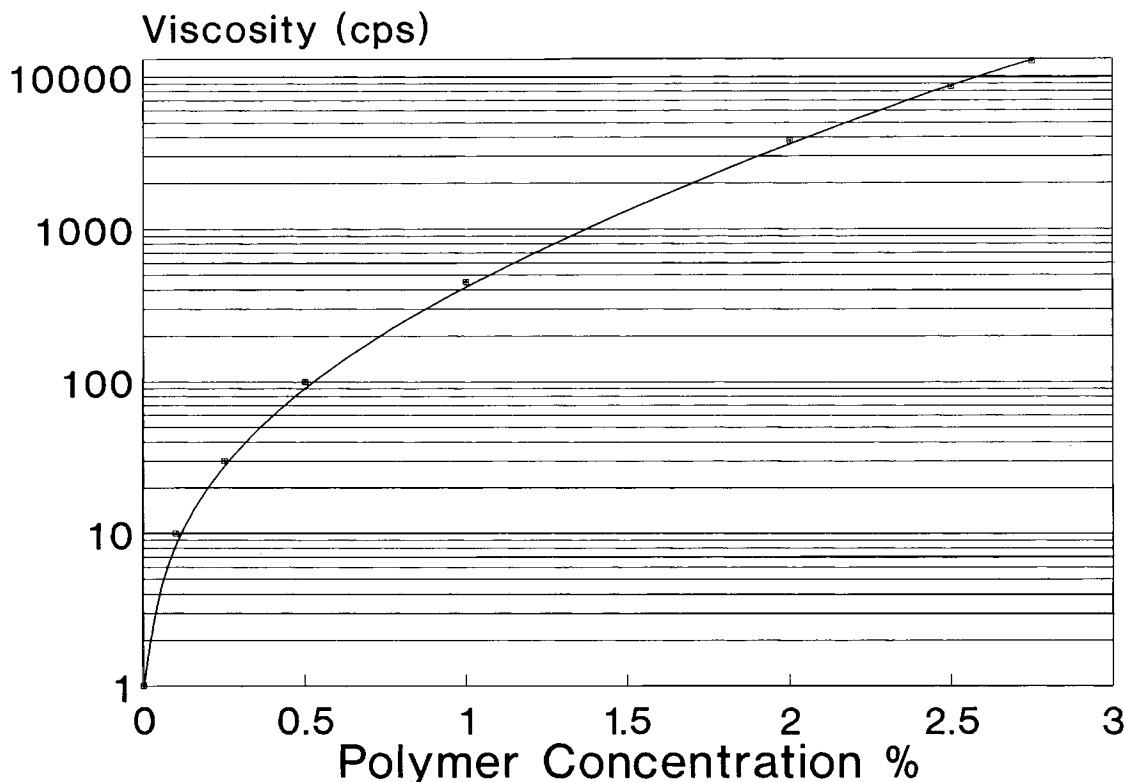
Figure 1   Viscosity of polyacrylamide in the presence of 50.0 g/L sodium hydroxide and 25.0 g/L sodium dithionite at 25°C.

concentration of polymer the diffusion of the dithionite ion radical is impeded, resulting in a slightly lower diffusion coefficient, D, and explaining the small but statistically significant increase in halftime that has been observed. It is expected that at even higher concentrations of polymer the diffusion coefficient will be decreased even more, as the aqueous medium more and more closely approaches a gel structure.

CONCLUSION

Analysis of the experimental results obtained in this investigation reveals that the beneficial, stabilizing effect of polyacrylamide on sodium dithionite that has been observed in commercial vat dyeing with 0.1–0.8 g/L of the polymer is due solely to the ability of the polymer to promote increased pickup of the reducing agent solution, resulting in a lower specific surface of the solution on the fabric and lower rates of decomposition of reducing agent. When the concentration of polymer is increased to levels not usually employed in practice, e.g., much above about 1.0 g/L, the polymer can bring about a further decrease in decomposition rates by impeding the diffusion of the dithionite ion radical in the aqueous solution.

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