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REDUCTION OF SALT REQUIREMENTS IN DYEING COTTON WITH FIBER REACTIVE DYES

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Large quantities of sodium chloride (NaCl) or sodium sulfate (Na_2SO_4) are used in the exhaust dyeing of cellulose with fiber reactive dyes. Many traditional fiber reactive dyes require 50 - 100 g/L of the salts to promote adequate exhaustion. Even with the large quantities of water required for rinsing the dyeings, the effluent still averages 2000 - 3000 ppm NaCl when it is used [1]. This level exceeds the current toxicity limit for NaCl established by the U. S. Environmental Protection Agency, and many dyers are discharging at or above this level [2]. Recent attempts to lower the levels of NaCl or Na_2SO_4 in waste water effluent have involved the selection of dyes with higher affinity for cellulose and dyeing at lower liquor ratios [3]. Also, many dyestuff manufacturers have developed a line of fiber reactive dyes that require less salt to promote exhaustion [4]. Neither of these efforts has proven to be totally satisfactory. This work was undertaken to explore the use of other compounds for promoting exhaustion and fixation of fiber reactive dyes on cellulosic fibers.

Experimental

10.0 g bleached cotton skeins from Testfabrics, Inc. were used in all experiments. Unfinished C.I. Reactive Red 180 (Remazol Red F3B presscake, DyStar LP) was selected as a model dye for most experiments. Due to its high degree of sulfonation and water solubility (see Figure 1), this dye requires extremely large quantities of NaCl for adequate exhaustion. Any compound that promotes good exhasution of this dye should therefore be very effective with other fiber reactive dyes. C. I. Reactive Violet 5 (Remazol Brilliant Violet 5R, DyStar LP), C. I. Reactive Blue 21(Remazol Turquoise L-P, DyStar LP), and Remazol Turquoise Blue G (DyStar LP), were also used in some experiments.

All chemicals were reagent grade or better. Some carboxylic acid salts were not available commercially and were prepared in the laboratory by reaction of the acid with either sodium or potassium hydroxide. All concentrations of NaCl and compounds evaluated as potential replacements for it are given in normality (N), i.e., gram-equivalents per liter, so that cation concentrations are identical in comparable experiments. 1.711N NaCl is equivalent to 100 g/L NaCl.

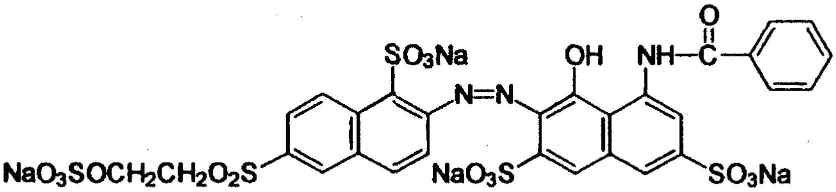

Figure 1. Structure of C.I. Reactive Red 180.

All dyeings were conducted on an Ahiba Texomat at 60°C and a liquor ratio of 20:1 according to the Hoechst-Celanese constant temperature method [5]. 2.0% dye (OWF) was used in all experiments with all of the dye and salt or salt replacement added to the bath initially. After 45 minutes, the alkali (5% Na_2CO_3 and 2% NaOH 50%) was added and dyeing continued for an additional 45 minutes. After dyeing, samples were given a thorough rinse with cold water followed by a warm water rinse, a hot water wash with detergent at 100°C, and final cold water rinse.

Dyebath exhaustion studies were conducted using a Perkin-Elmer uv-vis spectrophotometer Model 559A with a flow through cell attachment. The concentration of dye fixed in the fiber was determined spectrophotometrically by dissolving dyed skeins in 70% H_2SO_4 and determining the dye concentration in solution using a Cary 3E uv-vis spectrophotometer. Where K/S values are reported, reflectance measurements were obtained on a Macbeth Color-Eye Model M2020PL.

Results and Discussion

Cationic Surfactants

A series of n-alkyltrimethylammonium bromides with alkyl chain lengths of C_6, C_8, C_{10}, C_{12}, C_{14}, and C_{16} was investigated to determine the potential for cationic surfactants to promote exhaustion and fixation of fiber reactive dyes. All surfactants were evaluated at fractional concentrations up to their critical micelle concentration (cmc) and at twice their cmc. Skeins were treated with the surfactant solution at the dyeing temperature for 20 minutes prior to the addition of the dye. The C_{14} and C_{16} surfactants promoted rapid and nearly complete (95%) exhaustion of the dye at a concentration of 1/16 cmc, while the lower alkyl chain length surfactants promoted little exhaustion (< 35%) at any concentration. Representative exhaustion curves are shown in Figure 2. Fixation was poor for all surfactants at all concentrations (<0.3 mg dye/g fiber in all cases), however, as most of the exhausted dye was removed during rinsing. The theoretical maximum dye fixation is 4.0 mg/g. Fixation of C. I. Reactive Red 180 for all concentrations of each surfactant is illustrated in Figure 3.

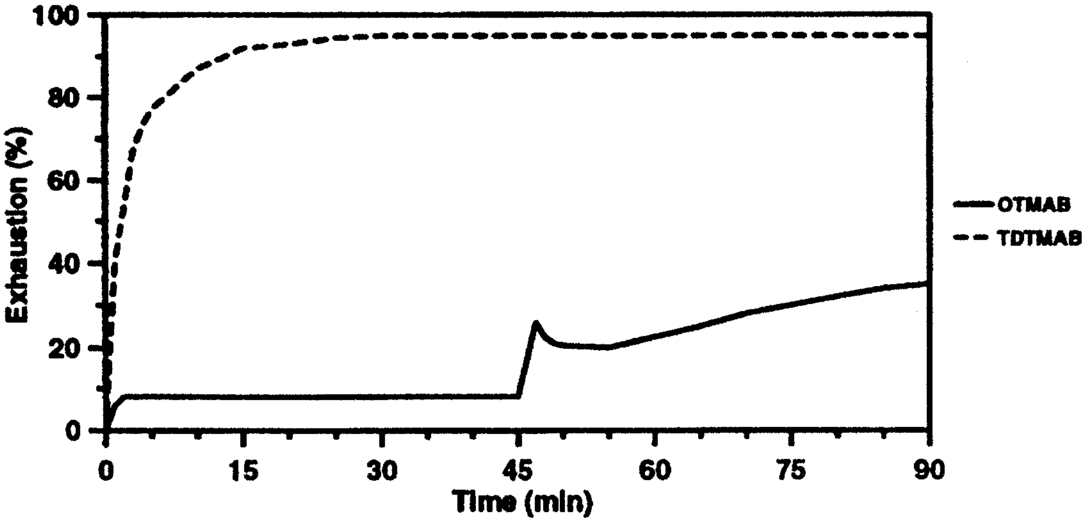

Figure 2. Exhaustion of C.I. Reactive Red 180 on cotton in presence of octyltri- methylammonium bromide (OTMAB) and tetradecyltrimethylammonium bromide (TDTMAB). Surfactant concentrations are 1/16 of their respective critical micelle concentrations (cmc).

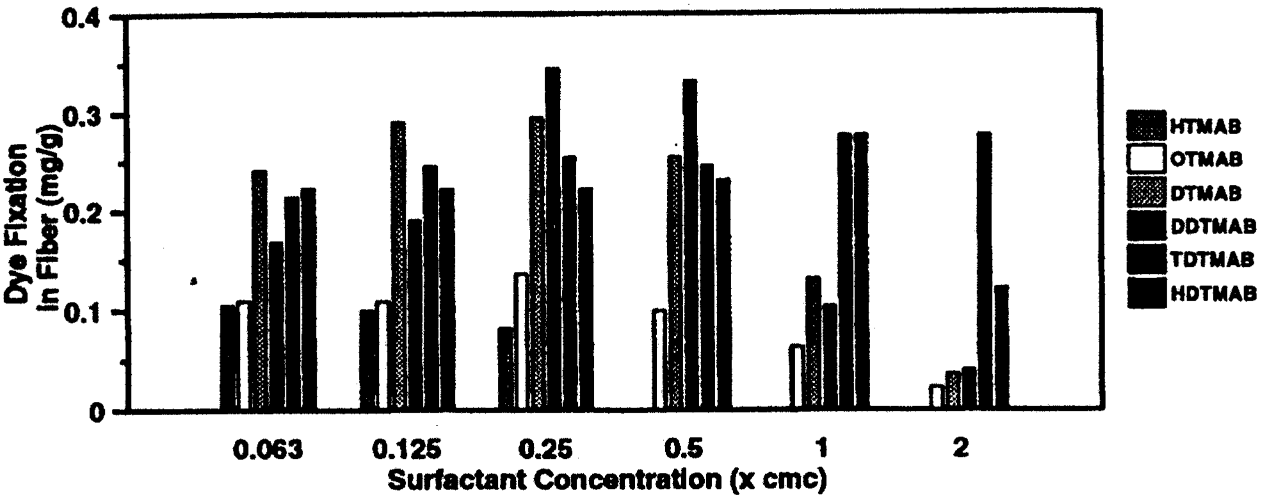

Figure 3. Fixation of C.I. Reactive Red 180 with various concentrations of alkyltrimethylammonium bromide surfactants. Alkyl groups: HTMAB = hexyl, OTMAB = octyl, DTMAB = decyl, DDTMAB = dodecyl, TDTMAB = tetradecyl, and HDTMAB = hexadecyl.

UV/Vis studies showed that the C_{14} and C_{16} surfactants interact with the dye, and after standing for one hour appreciable precipitation of the dye occurs. This behavior was not observed in dye solutions containing the lower alkyl chain length surfactants. It is hypothesized that the C_{14} and C_{16} surfactants are adsorbed onto the fiber surface during the pretreatment but the lower alkyl chain length surfactants are not. The adsorbed surfactant molecules attract dye molecules to the fiber surface where an ion-association compound is formed between the surfactant and dye. The resulting compound is too large to diffuse into the fiber or has little affinity for the fiber and is thus removed in rinsing.

Group IA, IIA, and IIIA Chlorides

Chlorides of Group IA (Li, Na, K, and Cs), IIA (Ca, Mg, and Ba), and IIIA (Al) metals were evaluated to determine if other alkali metal cations were more effective than sodium in promoting exhaustion and fixation. All salts were evaluated at concentrations of 0.3422, 0.6844, 1.027, 1.369, and 1.711N. In general, Group IIA and IIIA chlorides were found to be unsuitable for dyeing with fiber reactive dyes. They promoted exhaustion but formed their insoluble alkali metal hydroxides on addition of alkali. In addition to the large quantity of precipitate in the dyebath, fixation was poor due to consumption of alkali in forming the insoluble salts.

For the Group IA chlorides, exhaustion and fixation increased with concentration. The fixation results are illustrated in Figure 4. Fixation increased with atomic size of the cation, i.e., $Cs^+ > K^+ > Na^+ > Li^+$, and equal fixation was obtained with about 20 g/L less of KCl and about 40 g/L less of CsCl compared to NaCl. Similar results have been reported in the literature for the exhaustion of direct dyes on cotton [6,7,8], and the increased exhaustion has been attributed to such factors as decreasing surface (zeta) potential of the cotton fiber [6], increasing ion-exchange between counterions of the dye and electrolye in the bulk solution [7], and increasing water structure breaking properties of the ions [8].

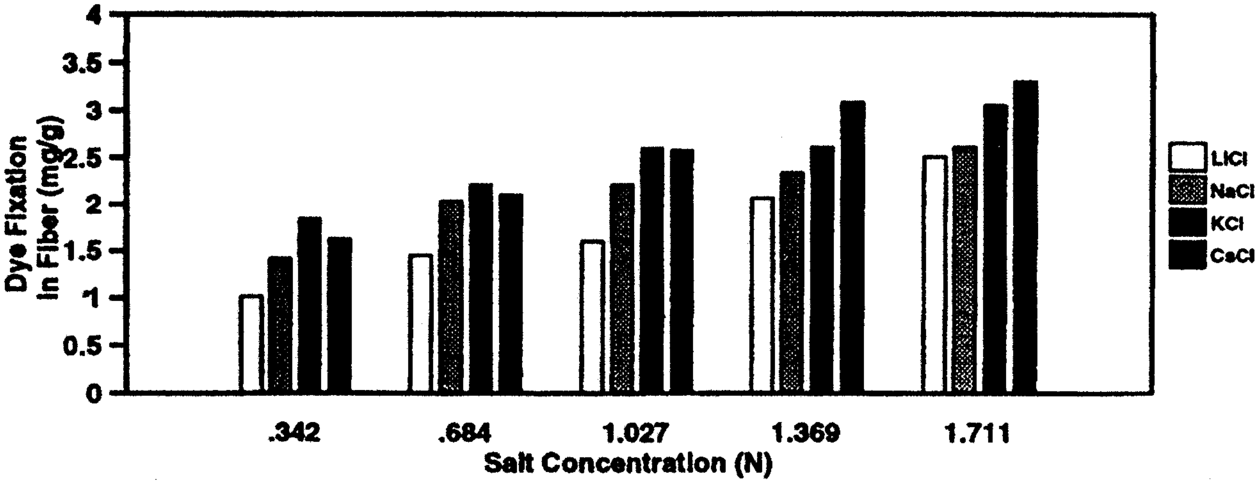

Figure 4. Fixation of C.I. Reactive Red 180 with various concentrations of Group 1A chlorides.

It should be noted that the fixation obtained with KCl is on average 17% higher than that obtained with NaCl. The use of potassium instead of sodium salts as the electrolyte to promote exhaustion and the alkali for fixation may therefore substantially reduce the amount of salt requirement in dyeing with fiber reactive dyes.

Salts of Carboxylic Acids

Sodium and potassium salts of various carboxylic acids were also evaluated for their potential to promote exhaustion and fixation of fiber reactive dyes on cotton. The salts evaluated included those of (1) the monocarboxylic acids formic, acetic, and benzoic; (2) the dicarboxylic acids oxalic, malonic, succinic, tartaric, itaconic, adipic and phthalic; (3) the tricarboxylic acids citric and 1,2,4-benzenetricarboxylic; and (4) the tetracarboxylic acids butanetetracarboxylic and 1,2,4,5-benzenetetracarboxylic.

The fixation obtained with sodium salts of monocarboxylic acids is illustrated along with that for NaCl in Figure 5. Except for sodium benzoate, fixation increased with concentration and, in general, was higher than that obtained with equivalent concentrations of NaCl. The best results were obtained with sodium formate. It is a promising replacement for NaCl as fixation at 1.369N (2.72 mg/g) is higher than that obtained with 1.711N NaCl (2.61 mg/g). The unusual results obtained with sodium benzoate are difficult to explain as the other aromatic carboxylic acid salts evaluated promoted higher fixation than NaCl and KCl (see Figures 6 - 8).

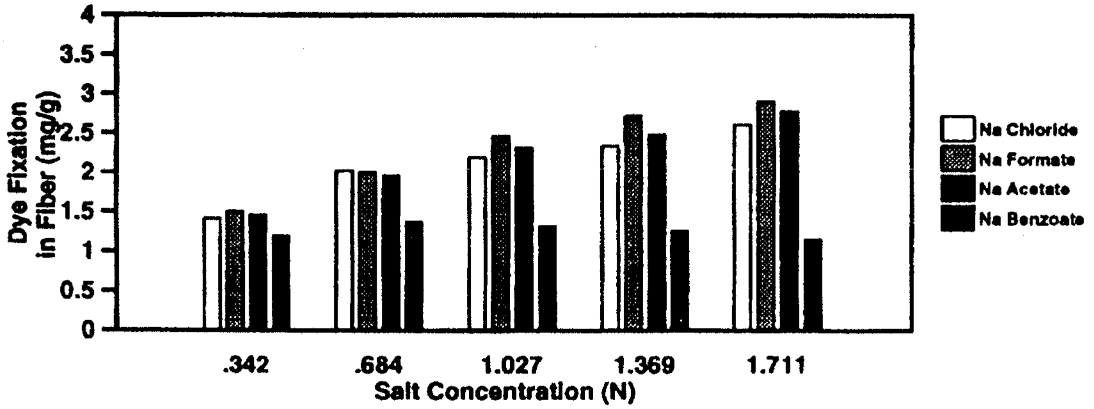

Figure 5. Fixation of C.I. Reactive Red 180 with various concentrations of sodium salts of monocarboxylic acids.

Fixation results for potassium salts of some dicarboxylic acid compared to KCl are illustrated in Figure 6. Fixation increased with concentration to a maximum at 1.369N. In general, the three salts illustrated all promoted higher fixation than KCl. Of these salts potassium phthalate was the most effective. Fixation with 1.027N (3.05 mg/g) is equivalent to that with 1.711N KCl and 17% higher than that obtained with 1.711N NaCl (2.61 mg/g).

Salts of tricarboxylic acids also promoted a higher degree of fixation than the simple inorganic salts. The results for potassium citrate and the tripotassium salt of 1,2,4-benzenetricarboxylic acid (KBTriCA) are given along with KCl in Figure 7. The fixation obtained with these two salts was, in general, comparable to each other; and both promoted slightly higher fixation at each concentration than that obtained with KCl. Fixation was significantly higher than that obtained with NaCl, however.

The full potassium salts of butanetetracarboxylic acid (KBTCA) and 1,2,4,5-benzenetetracarboxylic acid (KBTetCA) were evaluated as tetracarboxylic acid salts.

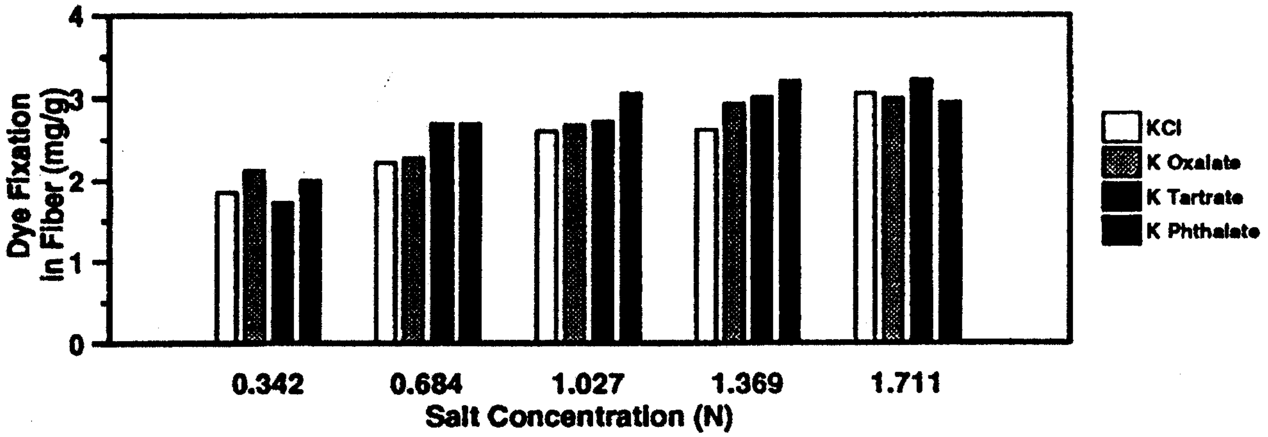

Figure 6. Fixation of C.I. Reactive Red with various concentration of potassium salts of dicarboxylic acids.

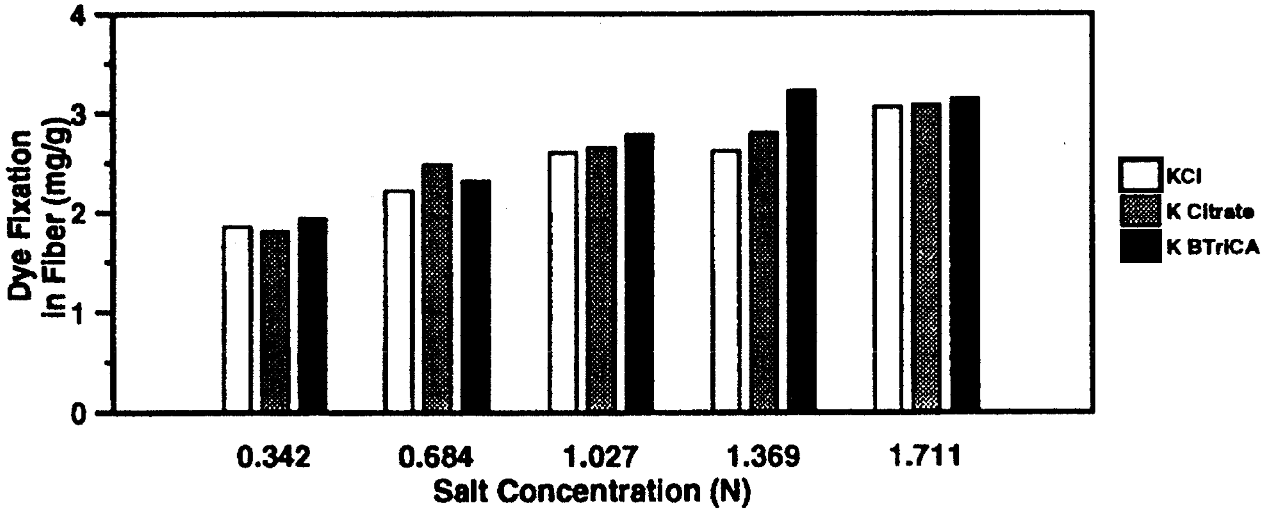

Figure 7. Fixation of C.I. Reactive Red 180 with various concentrations of potassium salts of tricarboxylic acids. KBTriCA = tri salt of 1,2,4-benzenetricarboxylic acid.

Fixation obtained with these salts compared to KCl are given in Figure 8. The KBTetCA promoted a higher degree of fixation than KBTCA at all concentrations. Except for the 0.342N level, both salts promoted significantly higher fixation than KCl at the same normal concentrations. The fixation obtained with 1.711N NaCl is obtained with only 0.684N of these salts.

Overall the carboxylic acid salts promoted exhaustion and fixation to a greater degree than NaCl. At the 1.711N concentration exhaustion was significantly higher and fixation at least 17% higher for the carboxylic acid salts. For most of these salts, fixation at the 1.027N level was higher than that obtained with 1.711N NaCl.

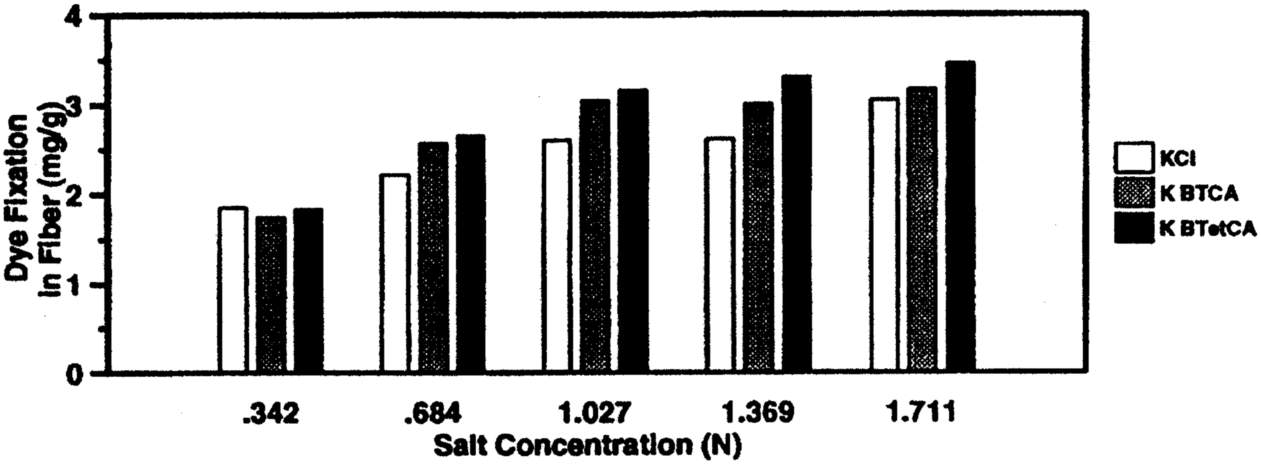

Figure 8. Fixation of C.I. Reactive Red 180 with various concentrations of potassium salts of tetracarboxylic acids. KBTCA = tetrasalt of butanetetracarboxylic acid, KBTetCA = 1,2,4,5-benzenetetracarboxylic acid.

Fixation, in general, increased with the number of carboxylate groups on the salts. The range of fixation obtained with compounds containing varying number of carboxylate groups at the 1.711N concentration is given in Table 1.

Table I. Fixation of C.I. Reactive Red 180 on cotton using mono-, di-, tri-, and tetracarboxylic acids to promote exhaustion.

No. Carboxylate Groups	Fixation (mg/g)
1	1.14 - 2.85
2	2.87 - 3.36
3	3.01 - 3.17
4	3.07 - 3.38

Except for the unusual behavior obtained with benzoate, the aromatic carboxylates in general promoted a higher degree of fixation than the aliphatic ones. Also potassium salts generally promoted a higher degree of fixation than sodium salts.

It was suspected that the carboxylate salts promoted greater dye aggregation than NaCl, but spectrophotometric analyses of dye solutions containing NaCl and sodium citrate did not confirm this. Nango[9] reported increased exhaustion of direct dyes on cotton when polyelectrolytes like sodium polyacrylate and sodium alginate or the sodium salt of galacturonic acid were substituted for NaCl. He too reported negligible interaction between the polyelectrolytes and dye, and attributed the increased exhaustion to a new transport mechanism.

Salt Substitute for Dyeing with Fiber Reactive Dyes

From the results of these studies, the authors propose the use of sodium citrate to reduce or eliminate the use of of NaCl and Na_2SO_4 in dyeing with fiber reactive dyes. Although citrate did not produce the highest degree of fixation of the compounds evaluated, it is readily available in large quantities, biodegradable, has been traditionally used in textile wet processing, and promotes much higher fixation than NaCl. Figure 9 illustrates the primary and secondary exhaustion obtained with 1.711N sodium citrate compared to 1,711N NaCl. Primary exhaustion is significantly higher with the citrate, and although secondary exhaustion is not as high, the final exhaustion is still higher. The most significant difference is in fixation. Fixation is 3.24 mg/g with sodium citrate compared to 2.61 mg/g with NaCl.

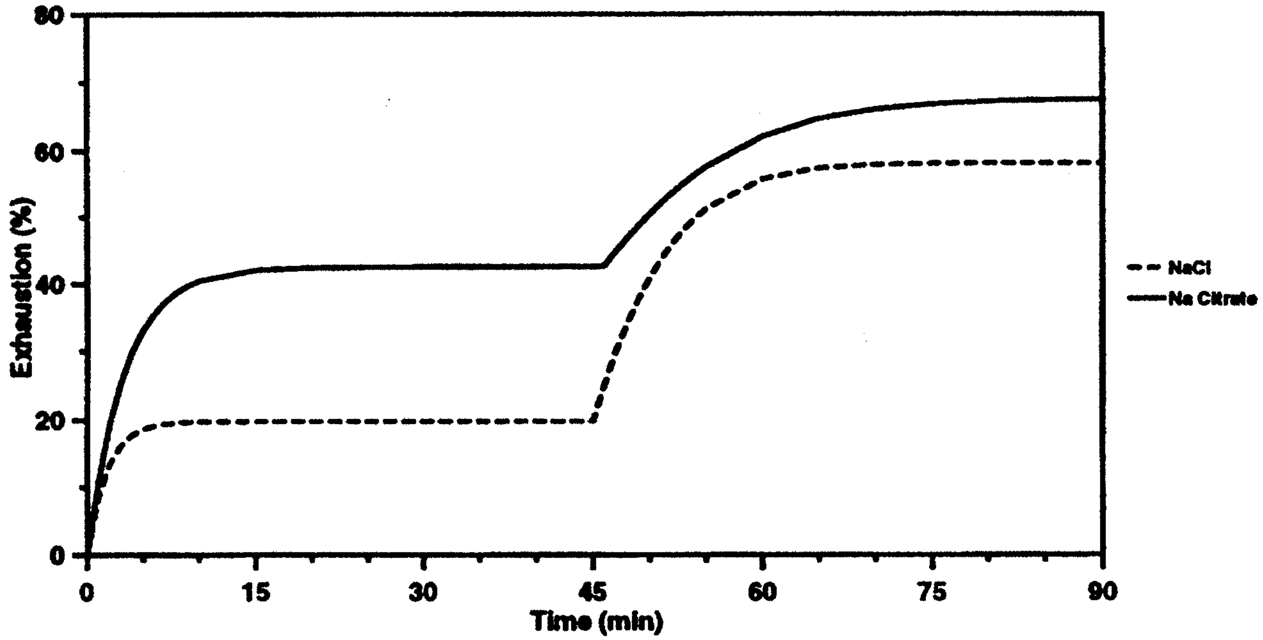

Figure 9. Exhaustion profile for C.I. Reactive Red 180 in presence of 1.711N sodium chloride and 1.711N sodium citrate.

Since citrate is a chelating agent, there is the possibility of it complexing with the metal ion of metal complex fiber reactive dyes and causing a decrease in dye strength or even a color change. To determine if this would occur, dyeings were made with 1.711N NaCl and 1.711N sodium citrate using the following metal complex dyes: (1) C.I. Reactive Violet 5, (2) C.I. Reactive Blue 21 and (3) Remazol Turquoise Blue G. The shade and fixation with citrate were compared to those with NaCl for each dye. In each case there were no shifts in the reflectance spectra of the dyeings. This indicates that substituting sodium citrate for NaCl does not affect the shade of metal complex fiber reactive dyes. The Kubelka-Monk K/S values at the wavelength of maximum absorption for the dyeings are illustrated in Figure 10. Using the K/S values as an indication of dye fixation, there is no adverse effect on dye strength caused by using sodium citrate. Fixation is higher with sodium citrate for all three dyes, and it is significantly higher for the turquoise dyes.

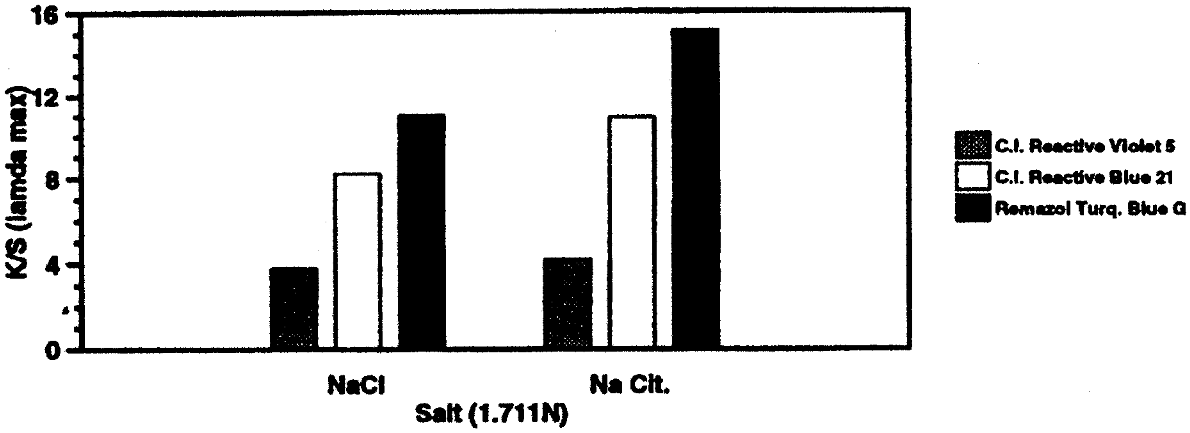

Figure 10. Fixation as measured by K/S of metal complex fiber reactive dyes on cotton with sodium chloride and sodium citrate.

Conclusions

Cationic surfactants, Group IA, IIA, and IIIA chlorides, and carboxylic acid salts have been investigated as potential replacements for sodium chloride in dyeing cotton with fiber reactive dyes. Cationic surfactants are not an alternative as those that promote exhaustion produce only surface exhaustion and thus low fixation. Group IIA and IIIA chlorides precipitate under the alkaline condition required for fixation and are thus not viable alternatives. Potassium and cesium chloride promote higher exhaustion and fixation and are potential replacements. The best results are obtained with di-, tri-, and tetracarboxylic acid salts. These compounds promote much higher exhaustion and fixation than sodium chloride. Sodium citrate is a very effective replacement for sodium chloride.

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