The Effect of Aluminum Hydroxide Dissolution on the Bleeding of Aluminum Lake Dyes

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The effect of pH on the bleeding of FD&C yellow No. 5 aluminum lake and FD&C red No. 40 aluminum lake was investigated. The pH–bleeding profiles corresponded to the pH–solubility profile of aluminum hydroxide. The similarity of the bleeding profiles of both lake dyes and the pH–solubility profile of aluminum hydroxide indicates that pH related bleeding, other than that occurring by competition with anions, is a result of dissolution of the aluminum hydroxide substrate. This dissolution is related to the properties of the substrate rather than to the structure of adsorbed dye.

KEY WORDS: lake dyes; aluminum hydroxide dissolution; lake dye bleeding.

INTRODUCTION

A lake dye can be defined as a pigment that is prepared by precipitating a soluble dye as a metallic salt in the presence of an inert substrate, the latter forming an integral part of the product (1). The substrate may be aluminum oxide or hydroxide, clay, titanium dioxide, zinc oxide, talc, or calcium carbonate. Currently, aluminum oxide and aluminum hydroxide are the only approved substrates for preparing FD&C lake dyes (2). Lake dye formation renders the dye essentially insoluble. Lake dyes are therefore used as colorants in film coating in order to overcome problems of migration of soluble dyes within the film coat. Lake dyes impart color to a film coat by being dispersed uniformly in the coating. Therefore the particulate properties such as size, shape, and size distribution are important (3). It is also essential that the dye should not desorb or dissolve. The desorption or dissolution of the dye from the lake dye is referred to as "bleeding." This release of the dye will result in an uneven distribution of the color in a film coat. Consequently, a mottled appearance results.

Competition with other anions has been shown to cause desorption of the dye from aluminum hydroxide or oxide substrates (4,5). Mishra *et al.* (4) studied the effect of sodium nitrate, sodium sulfate, and sodium phosphate (0.0001–0.1 *M*) on desorption of anionic dyes from an aluminum oxide substrate and found that the desorption efficacy was in the order of phosphate > sulfate > nitrate. Yashushi Kubo *et al.* (5) studied the bleeding of tartrazine from the aluminum lake dye in a sodium chloride solution. They concluded that the bleeding was occurring due to an anion-exchange reaction between the chloride and the dye anions. In a subsequent study, the same authors showed that bleeding of the lake dye in a sodium chloride solution is influenced by the method of manufacture of the aluminum lake dye (6).

The pH of the solution must be considered when choosing a colorant as the pH may have a large influence on the stability of the organic dye molecules and the lake dyes. The published stability data for the organic dyes related to pH are qualitatively stated and difficult to interpret. The dyes, tartrazine and allura red, which are used to prepare FD&C yellow No. 5 aluminum lake and FD&C red No. 40 aluminum lake, respectively, show no appreciable change in color in the pH range of 3.0–8.0 (2). However, there is little information available regarding the pH stability of aluminum lake dyes. Since the pH affects the solubility of aluminum oxide or hydroxide, it is likely that the pH will affect the stability, especially bleeding, of the lake dye.

The effect of pH on the aqueous solubility of aluminum oxide or hydroxide has been studied extensively (7–11). Aluminum oxide and hydroxide are very soluble at both low and high pH levels. At an acidic pH, aluminum hydroxides or oxides produce soluble $Al(OH_2)_6{}^{3+}$. The solubility of aluminum in alkaline solutions is due to the formation of $Al(OH)_4{}^-$. Aluminum is particularly insoluble at pH 5–6 as a result of the formation of the stable hydroxide complexes. The effect of pH on the bleeding of aluminum lake dyes was studied and attempts were made to relate it to the solubility of the substrate.

MATERIALS AND METHODS

The samples of FD&C yellow No. 5 aluminum lake with a pure dye content of 38% (Lot No. AD 8826, Warner Jenkinson) and FD&C red No. 40 aluminum lake with a pure dye content of 40% (Lot No. AF 1327, Colorcon) were commercial material. All other chemicals used were either analytical grade or reagent grade and were used without further modification or purification.

Two hundred-milliliter suspensions of each of the lake dyes were prepared at suitable volume fractions. The suspensions were adjusted to the required pH with either 0.01 *M* KOH or 0.01 *M* HNO_3 and allowed to equilibrate at room temperature. Unless otherwise stated, the volume fraction of the lake dyes in the suspension was 6.06×10^{-6} (0.0012%, w/v). Aliquots of 10 mL were withdrawn at regular time intervals from the suspensions. These aliquots were filtered through a 0.2-μm cellulose acetate membrane filter (Nalgene disposable syringe filter) and the filtrate was assayed for dye and aluminum.

The amount of the dye dissolved from the lake dye was monitored using visible spectrophotometry. A Beer's law standard curve for both FD&C yellow No. 5 and FD&C red No. 40 was prepared. The standard curves were constructed for FD&C yellow No. 5 over the concentration range of 0.18

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to 9.0 mg/mL and for FD&C red No. 40 from 0.182 to 1.82 mg/mL. The absorbance was measured using a single-beam spectrophotometer (Beckman DU-7) in 1-cm silica cells. The readings were taken at 426 nm for FD&C yellow No. 5 and at 506 nm for FD&C red No. 40. As the bleeding studies were conducted over a range of pH values, the standard curves for FD&C yellow No. 5 and FD&C red No. 40 were constructed at each pH at which the studies were undertaken. The concentration of dye in the samples was determined from the standard curves of each of the dyes at the corresponding pH. The UV absorbances of solutions of FD&C yellow No. 5 or FD&C red No. 40 was not affected by pH in the pH range studied.

The graphite furnace atomic absorption method was used to determine the concentration of aluminum in solution. The atomic absorption system (Varian GTA-96) was equipped with a microprocessor-controlled spectrophotometer and a graphite furnace. An aluminum hollow cathode lamp was utilized as the light source. Pyrrolytically coated graphite tubes were used as the atomizer. An auto sampler system with a sample volume of 30 μL was used to give reproducible sample volumes. Spectrophotometer settings included a wavelength of 309.3 nm, a lamp current of 10 mA, a window slit of 0.5 nm, a measurement time of 3.2 sec, and measurement of the sample absorbance without background corrections. The atomization temperature was set at 2500°C. The aluminum concentration was determined by calculating the peak areas. Four replicates were made for each of the measurements. The flow rate of the argon gas was adjusted to 3 L/min. Aluminum standards were prepared from a 1000 μg/mL aluminum reference solution (RICCA Chemical Company) by dilution with deionized distilled water and contained between 20 and 200 μg/mL of aluminum. A standard curve was used to determine the concentration of the dissolved aluminum.

RESULTS AND DISCUSSION

The bleeding of FD&C yellow No. 5 aluminum lake and FD&C red No. 40 aluminum lake was investigated as a function of pH and time. Figure 1 shows the behavior of FD&C red No. 40 aluminum lake. The results for FD&C yellow No.

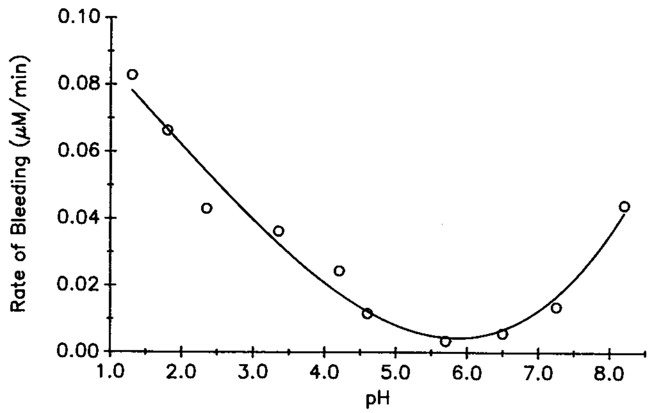

Fig. 2. Relationship between pH and zero-order rate constant for the bleeding of FD&C yellow No. 5 aluminum lake at volume fraction 6.06×10^{-6} (0.0012%, w/v) and 25°C.

5 aluminum lake were very similar. The studies were conducted over a pH range of 2–8. The results show that the extent of bleeding is pH dependent for both lake dyes and that the concentration of dye in solution increases with time. The bleeding profiles of the two lake dyes at 1 and 2 hr are very similar. There was minimum bleeding between pH 5 and pH 6. The similarity of the pH–bleeding profiles of the two different lake dyes suggests that the bleeding of the lake dyes is not related to the structure of the absorbed dye.

The rate of bleeding of FD&C yellow No. 5 aluminum lake at a volume fraction of 6.06×10^{-6} (0.0012%, w/v) was also investigated over a range of pH conditions. The rate of bleeding at all pH conditions studied appears to follow zero-order kinetics for the concentration range studied. In Fig. 2, the zero-order rate constants for bleeding are plotted against the pH. The minimum rate constant for bleeding occurred at pH 5.7.

The pH–rate of bleeding profile (Fig. 2) also resembles the pH–solubility profile of aluminum hydroxide (7). Therefore, it is likely that the bleeding of the lake dyes observed in Figs. 1 and 2 is related to the dissolution of the aluminum hydroxide substrate. The faster rate of dissolution of the aluminum hydroxide substrate at low pH probably accounts for the enhanced rate of bleeding below pH 4.0. At and

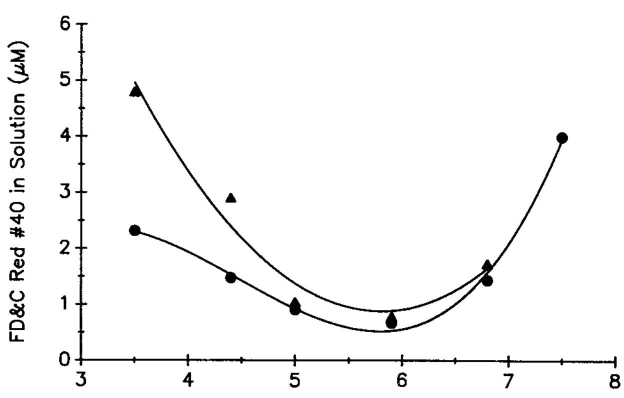

Fig. 1. Effect of pH and time on the bleeding of FD&C red No. 40 aluminum lake at volume fraction 6.06×10^{-6} (0.0012%, w/v) and 25°C. ●, 1 hr; ▲, 2 hr.

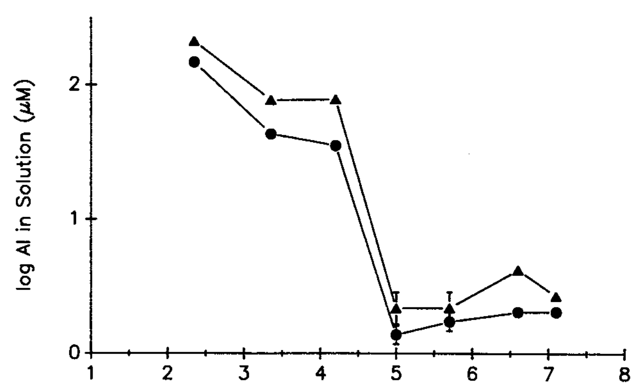

Fig. 3. Effect of pH on the dissolution of aluminum from FD&C yellow No. 5 aluminum lake at volume fraction 3.03×10^{-5} (0.006%, w/v) and 25°C. ●, 1 hr; ▲, 2 hr.

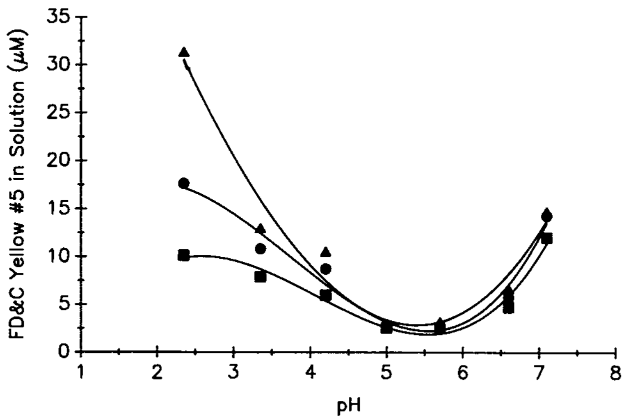

Fig. 4. Effect of pH on the bleeding of FD&C yellow No. 5 lake at volume fraction 3.03×10^{-5} (0.006%, w/v) and 25°C. ■, 0.5 hr.; ●, 1 hr; ▲, 2 hr.

above pH 7.25, any bleeding in excess of that caused by the dissolution of aluminum hydroxide is probably due to a change in the ionization state of the dye.

In order to substantiate this hypothesis, the amount of aluminum which dissolved from FD&C yellow No. 5 aluminum lake in 1 or 2 hr was determined. At a volume fraction of 6.06×10^{-6} (0.0012%, w/v), there was not enough aluminum in solution after 2 hr to be measured by the graphite furnace atomic absorption technique for all pH conditions. The volume fraction was therefore increased to 3.03×10^{-5} (0.006%, w/v). The concentration of aluminum in solution after 1 or 2 hr could be determined in this suspension as a function of pH. Figure 3 gives the pH–aluminum solubility profiles at 1 and 2 hr. The minimum solubility occurs between pH 5 and pH 6. The increase in the concentration of aluminum in solution with time also agrees with the pH–solubility profile of aluminum hydroxide (7) as the aluminum concentration is below saturation. The concentration of FD&C yellow No. 5 in solution was also determined for these suspensions. The pH–bleeding profile that was obtained (Fig. 4) also had a minimum between pH 5 and pH 6. In addition, the concentration of FD&C yellow No. 5 in solution increased with time.

Thus, it is concluded that dissolution of the aluminum hydroxide substrate of aluminum lake dyes produces bleeding, especially if the pH of the lake dye suspension differs from the pH of minimum solubility of the aluminum hydroxide substrate.

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