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Predicting the Precipitation of Acid and Direct Dyes in Natural Waters*

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ABSTRACT

A simple screening test was used to determine whether acid and direct dyes precipitate at calcium concentrations typical of hard waters in the Southeastern Piedmont region of the United States. Of 52 dyes tested, only three direct dyes (Direct Black 19, Direct Black 22, and Direct Blue 75) and seven acid dyes (Acid Red 88, Acid Red 114, Acid Red 151, Acid Brown 14, Acid Black 24, Acid Orange 8, and Acid Blue 113) precipitated. Structures of all but three of the dyes, or ligands in the case of complexes, are in the literature.

Conditional solubility-product constants (K_{sp}) *of calcium salts were also determined by titrimetric and batch-equilibration methods for five of the dyes (Acid Red 114, Acid Red 151, Acid Orange 8, Acid Blue 113, and Direct Yellow 28). The* K_{sp} *values range from* 3×10^{-10} *to* $1{\cdot}0 \times 10^{-7}$ M^2 *and from* 6×10^{-15} *to* 1×10^{-9} M^3 *for salts of divalent and monovalent dyes, respectively.*

Monitoring data show that maximum calcium concentrations in Southeastern Piedmont waters are approximately 2×10^{-3} *M and thus unlikely to*

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precipitate most dyes of the types represented. However, it is not known whether these conclusions are valid for newer dyes that have structures not reported in the open literature.

1 INTRODUCTION

At present, few scientifically defensible statements can be made regarding the fate or effects of any dye in an aquatic environment. Indeed, there are hardly any published data on concentrations of dyes in natural waters, and there is even less information on long-term toxicities. Because of the large number of dyes, their widespread use, diversity of structures, and cost of studies, this situation is not likely to change dramatically. Thus, there is a need for methodologies that provide data that can be reliably extrapolated to other dyes and environments. For dye salts that may precipitate in natural waters, solubility-product constants and water composition can be used to predict maximum dissolved-dye concentrations in many different aquatic systems.

The specific goal of this study was to determine whether the dissolved concentrations of acid or direct dyes can be limited by precipitation as salts on discharge to streams. Attention was given to the Piedmont region of the South-eastern United States because of its high concentration of textile industries and consequent significant dye use. Addressing this dye-precipitation question requires data or assumptions about the following: (i) calcium concentrations in the receiving water, (ii) dye concentrations in the receiving water, (iii) solubility or solubility-product constant for the Ca dye salts, (iv) pH of the receiving waters, and (v) dependence of solubility on pH.

2 BACKGROUND

2.1 Dye properties

Surprisingly, except for alkali-metal compounds, hardly any data exist in the chemical literature on solubilities of sulfonated dye salts. The only reported dye-salt solubilities are from a 1929 study by Holmes[1] on several fluorescein stains, all of which were carboxylates. His data show that the sodium salts are much more soluble than the alkaline-earth salts. The data also confirm that, as expected, Ca salts are less soluble than corresponding Mg salts when the anion is much larger than the cation.[2] Similarly, detergents and other sulfonic acid derivatives[3,4] form insoluble salts of alkaline-earth or heavy metals.

Poor solubility of acid and direct dyes has long been a problem for both the dye manufacturer and the dyer. For this reason, dyes are usually prepared and used as soluble alkali-metal sulfonates. Solubility of a given metal salt, however, increases with the number of charges on the dye. For any given pH range, solubility will be constant if the sulfonate groups are completely ionized and if ionization of the amino and aromatic OH groups is constant. Further, if sulfonate groups are completely ionized, solubility will be minimal when ionization of other groups is minimal.

Ender and Müller[5] and Elöd and Frölich[6] have published data showing that sulfonate groups on acid and direct dyes are highly dissociated at pH's greater than about 1–3. Reeves and Kaiser[7] have reported negative pK_a's for several simple sulfonated dyes.

Amino- and OH-group pK_a's have been reported in only a few cases for dyes. As would be expected, they usually are less than 4 and greater than 8, respectively. This is consistent with the few pK_a's that we have found for acid and direct dyes. Haag and Mill[8] reported pK_a's for six of the dyes used in this study. Thus it is highly probable that the sulfonic acid groups of acid and direct dyes are almost completely ionized between pH 5 and pH 8, whereas other functional groups remain largely un-ionized.

2.2 Water characteristics

Although it is common knowledge that a pH range of 5–8 is typical of fresh surface water, many other parameters are less well known. Concentrations of some metals in river waters have been summarized by Stumm and Morgan[9] and Butler[10]. The data show that the dominant, non-alkali, cationic metals in surface waters are Ca and Mg and the ionic strength is relatively constant[10] at about 2×10^{-3} M. On the average, Ca is present at approximately twice the concentration of Mg. These facts led to the suggestion that precipitation as alkaline-earth salts might control the fate of dyes,[11] or other large organic anions, after their release to natural waters.

To make this work specific to the Piedmont region, data were obtained for an area that lies approximately between Dalton and Athens, GA, on the west, and Charlotte, NC, on the east.

For this area, the US Environmental Protection Agency's STORET[12] database contains information on environmental concentrations measured between 1980 and 1987. Data for Ca, Mg, and pH consisted of 727, 656, and 719 measurements, respectively, for approximately 120 different streams and lakes. The data show that, in virtually all cases, the Ca concentration is higher than that of Mg. The difference was nearly always greater than a factor of two, and usually much greater. Out of the 727 measurements of Ca concentration, only six exceeded 40 mg/liter (10^{-3} M). The six values ranged from 41·7 mg/liter (Cedar Creek, Bartow, GA) to 76 mg/liter (Dry Creek, Jackson, AL). Most often, Ca concentrations were closer to 4 mg/liter than to 40 mg/liter. Thus the highest Ca concentrations expected in Piedmont waters are between about 10^{-3} M and 2×10^{-3} M.

Hydrogen-ion concentrations, as expected, vary much more than those of the metals. Still, the STORET data show that 65% of the waters had pH's between 6 and 8; 95% were between 5 and 8.

The STORET data on metals are consistent with concentrations measured by Cherry[13] in an earlier study of North-west Georgia streams. He also reports a narrow pH range (7·1–7·8) for these streams.

Significantly, hardly any published data are available on specific dye concentrations in natural waters. Tincher[14,15] has reported a number of acid dyes in the Coosa River basin (GA) at levels of a few μg/liter to more than 150 μg/liter. Richardson and Waggott[16] have reported Acid Blue 1 in the River Thames at the low-microgram-per-liter level. Burg *et al.*[17] summarized work showing that fluorescent whitening agents have been found in river waters in the low-microgram-per-liter range. Solubilities of any of these compounds have been considered in only one study.[18] In that case, it was dismissed as a factor in the loss of fluorescent whitening agent from a Japanese river.

3 MATERIALS AND METHODS

3.1 Materials

All but four dyes used for this study were from press cake or unformulated colorant. They had been purified by repeated dissolution in dimethylformamide followed by precipitation with trichloroethylene. However, it should be noted that, for many of the 52 dyes studied, this process did not markedly increase purity as assayed by high-performance liquid chromatography and visible spectrophotometry. The purified dyes were supplied by courtesy of the US Environmental Protection Agency's Risk Reduction Engineering Laboratory, Cincinnati, OH, and were used as received. Only dyes having purities in excess of 90% and which precipitated in the screening test (see below) were used for the measurement of solubility-product constants. Four dyes were supplied by courtesy of Ciba–Geigy Corporation and were used as received, in the form of press cake.

Each dye, with the calcium salts used for solubility-product-constant measurements, was subjected to fast-atom-bombardment mass spectrometry. Negative-ion spectra were obtained with a VG model 70-SEQ mass spectrometer. In all cases but three (for which no structures are available), the resulting spectra were consistent with structures or data in the Colour Index.[19] Results of the mass spectrometry are being published separately.

Chemicals, other than water, were reagent grade or better. Water was purified by carbon filtration and ion exchange prior to use. Solid chemicals were dried *in vacuo* over anhydrous $Mg(ClO_4)_2$ to constant weight prior to use.

Unless otherwise noted, all experiments were conducted at an ionic strength of 3×10^{-3} M and pH 6. Whenever possible, this was accomplished through use, as solvent, of an ionic-strength solution. The ionic-strength solution was prepared from reagent grade KCl; pH was adjusted to 6 with HCl.

Stock solutions of Ca, 10^{-3} M, were prepared from $Ca(NO_3)_2 . 4H_2O$. If necessary, ionic strength and pH were adjusted with KCl and HCl, respectively.

3.2 Methods

A simple screening method was used to determine which dyes would not precipitate at Ca concentrations similar to those in natural waters. First, equal volumes of dye and $Ca(NO_3)_2$ solution were mixed. In this crude experiment, concentrations were approximately $2{\cdot}5 \times 10^{-3}$ M (100 mg/liter) and 0·01 M (400 mg/liter) for dye and Ca, respectively. The dyes were also subjected to a second, more carefully controlled test. For this purpose, 10^{-3} M calcium and dye solutions were prepared in the ionic-strength solution and the pH was adjusted, if necessary, to 6. Equal volumes of the solutions were mixed and allowed to stand overnight. The solutions were then centrifuged to determine whether precipitate had formed.

Solubility-product constants were determined by two independent techniques. The first was a batch-equilibration method. In this procedure, dye was first precipitated from water with calcium nitrate. The precipitate was washed repeatedly (suspended, shaken, and centrifuged) with ionic-strength solution, and the overlying water was discarded. This continued for from three to five washes or until it was clear that a portion of the salt had dissolved. The remaining salt was resuspended in ionic-strength solution and placed in a constant-temperature bath ($25 \pm 0{\cdot}1$°C) for at least 24 h. During this time, the suspension was gently agitated by motion of the bath water. In alternate experiments, the suspension was heated prior to placement in the 25°C bath.

On removal from the bath, the suspension was centrifuged and the Ca and dye concentrations were measured by ion-selective-electrode (ISE) and visible spectrophotometry, respectively.

The second method utilized potentiometric titration of Ca with dye. Both components were in ionic-strength solution at pH 6, and the Ca solution (0·001 M) was maintained at 25 ± 0·1°C while being purged with helium. The dye concentration in the titrant was approximately 0·01 M. Titration curves were analyzed by regression analysis and K_{sp} obtained by the method of Meites and Goldman.[20]

Because of concerns about the use of phosphate with calcium, and difficulties with ionic-strength control, all measurements were made in unbuffered solutions. In the case of the saturation method, we found that the pH did not deviate from 6 by more than 0·2 pH unit. The worst case observed for the titrimetric method was 0·3 pH unit. These variations produced no observed effect on the results.

3.3 Instruments

A Fisher Accumet Model 925 pH meter was used for both pH and potential measurements. An Orion Model 80-03, Ross Sure-Flow, reference half-cell was used to avoid precipitation of dye by mercury. The electrolyte in the electrode was 0·1M KNO_3. An Orion Model 93-20, calcium ISE and an Orion Model 91-01, pH half-cell were used for Ca-ion and pH determinations.

Calibration of the pH electrode was against standard buffer solutions, and measurements were temperature-compensated. The ISE was calibrated against known concentrations of $Ca(NO_3)_2$ in the ionic-strength solution. The calibration was used as a linear equation obtained by regression of the logarithm of concentration against potential (millivolts).

A Cary 210 spectrophotometer with 1-cm quartz cells was used to measure absorbance. Concentrations were obtained from a regression equation of absorbance (at the visible-absorption maximum) against known concentrations of dye in the ionic strength solution. The calibration curves were linear over the range used.

3.4 Calculations

Calculations are based on eqns (1)–(3) below. A slightly soluble dye salt of formula Ca_mD_n, in the absence of other sources of Ca^{2+} and D^{v-}, dissolves according to the equlibrium (eqn (1)) where $2m = nv$:

$$Ca_mD_n \rightleftarrows mCa^{2+} + nD^{v-} \tag{1}$$

For saturated solutions at constant ionic strength, the conditional solubility-product constant, K_{sp}, is given by eqn (2). Concentrations are used instead of activities, since ionic strength was constant and similar to that of the natural waters of interest.

$$K_{sp} = [Ca^{2+}]^m[D^{v-}]^n \tag{2}$$

Under these conditions, the molar concentration of a saturated dye-salt solution is given by eqn (3):

$$S = [K_{\mathrm{sp}}(m^{-m}n^{-n})]^{1/m+n} \tag{3}$$

4 RESULTS AND DISCUSSION

The screening test provides a simple method of determining whether anionic compounds will precipitate in natural waters. Although we did not do so, the procedure can also be used for K_{sp} determination from measurement of the anion alone. This requires that the solubility be much less than the concentration of the precipitating metal. Ionic strength and pH must also be controlled.

Table 1 gives the results of the first screening test in which 33 of 52 dyes did not precipitate. Of the 19 that did precipitate, 10 also precipitated in the second test. Dyes precipitated in the second screening test, in approximate order of amount of precipitate, were: Direct Blacks 19, 22 > Acid Red 114 > Acid Red 88, Acid Brown 14 > Acid Black 24 > Acid Orange 8 > Acid Red 151 > Acid Blue 113 > Direct Blue 75. There is no clear evidence whether Ca salts of acid or direct dyes are less soluble.

The second screening test simulates an environment having a Ca concentration of 10^{-3} M (40 mg/liter) to which dye is added at concentrations ranging from about 350 mg/liter to more than 1 g/liter. Although this Ca concentration is realistically high for the Piedmont, the dye concentrations are more than a thousandfold higher than those found by Tincher[14,15] in the Coosa River.

To assess better the behavior of dyes that did precipitate, solubility-product constants were determined for five of the dyes. The equilibrium constants for the five dyes are given in Table 2 as determined by two different methods.

Examination of data in Table 2 shows that the two methods give results differing by a factor of 1·3–3·5 and that the coefficients of determination of the averages range from 16 to 59%. Such agreement is much better than that often found for literature data and is more than adequate for environmental forecasts. Furthermore, the agreement between the two independent methods strongly suggests that there are no gross errors due to impurities, etc.

Interestingly, the Ca salts are much more soluble than might have been expected. The solubilities range from a high value of $3{\cdot}0 \times 10^{-4}$ M (200 mg/liter) for Acid Orange 8 to a low value of $1{\cdot}1 \times 10^{-5}$ M (10 mg/liter) for Acid Red 151. If these values are indicative of acid and direct dyes in general, we can assume that few of their Ca salts would have solubilities less than

TABLE 1
Results of First Screening Test

Dyes precipitated (19)

Acid dyes (8)

Light precipitate	*Heavy precipitate*
Orange 8, Red 114	Black 24, Blue 113
Red 337	Brown 14, Red 88, Red 151

Direct dyes (11)

Light precipitate	*Heavy precipitate*
Black 80, Violet 9	Black 19, Black 22
Blue 71, Blue 75	Yellow 28
Red 80, Red 81, Red 83, Yellow 106	

Dyes unprecipitated (33)

Acid dyes (23)

Black 1, Black 52
Blue 92, Blue 158
Green 20
Orange 7, Orange 10
Red 1, Red 14, Red 18, Red 57
Reed 27, Red 73, Red 183
Yellow 17, Yellow 23, Yellow 34
Yellow 151, Yellow 36, Yellow 49
Yellow 99
Violet 3, Violet 7

Direct dyes (10)

Blue 15, Blue 78, Blue 80
Blue 86, Blue 199, Blue 218
Red 24, Red 72, Red 254
Yellow 4

52 Dyes total

about $10^{-5}\ \mathrm{M}$. This concentration translates into solubility-product constants greater than $10^{-10}\ \mathrm{M}^2$ or $4 \times 10^{-15}\ \mathrm{M}^3$ for homovalent (CaD) and heterovalent (CaD_2) salts, respectively.

A stability diagram for Piedmont streams, Fig. 1, can be constructed by using a Ca concentration of $2 \times 10^{-3}\ \mathrm{M}$ (a little greater than the maximum) and low values of K_{sp} ($10^{-10}\ \mathrm{M}^2$ and $4 \times 10^{-15}\ \mathrm{M}^3$). The diagram shows the maximum dye concentrations attainable, under these conditions, without precipitation. At these extremes, CaD and CaD_2 salts would not precipitate unless the dye concentrations reached $5 \times 10^{-8}\ \mathrm{M}$ or $1{\cdot}4 \times 10^{-6}\ \mathrm{M}$, respectively. Based on the lowest molecular weights of these dyes (taken as 400), these dye concentrations would be at least 0·02 mg/liter and 0·56

TABLE 2

Conditional Solubility-Product Constants (K_{sp})

Calcium salt *(CaD_4)*	*Saturation method*	*Titration method*	*Average* *($n = 4$)*
Acid Blue 113	$3{\cdot}5 \times 10^{-8}\,\text{M}^2$	$4{\cdot}6 \times 10^{-8}\,\text{M}^2$	$4{\cdot}2 \times 10^{-8}\,\text{M}^2$
(CaD)	$3{\cdot}7 \times 10^{-8}\,\text{M}^2$	$4{\cdot}9 \times 10^{-8}\,\text{M}^2$	
Acid Orange 8	$5{\cdot}0 \times 10^{-11}\,\text{M}^3$	$1{\cdot}2 \times 10^{-10}\,\text{M}^3$	$9{\cdot}8 \times 10^{-10}\,\text{M}^3$
(CaD_2)	$5{\cdot}2 \times 10^{-11}\,\text{M}^3$	$1{\cdot}7 \times 10^{-10}\,\text{M}^3$	
Acid Red 114	$2{\cdot}1 \times 10^{-10}\,\text{M}^2$	$4{\cdot}9 \times 10^{-10}\,\text{M}^2$	$3{\cdot}4 \times 10^{-10}\,\text{M}^2$
(CaD)	$1{\cdot}4 \times 10^{-10}\,\text{M}^2$	$5{\cdot}0 \times 10^{-10}\,\text{M}^2$	
Acid Red 151	$3{\cdot}4 \times 10^{-15}\,\text{M}^3$	$7{\cdot}2 \times 10^{-15}\,\text{M}^3$	$5{\cdot}6 \times 10^{-15}\,\text{M}^3$
(CaD_2)	$4{\cdot}0 \times 10^{-15}\,\text{M}^3$	$7{\cdot}8 \times 10^{-15}\,\text{M}^3$	
Direct Yellow 28	$1{\cdot}2 \times 10^{-7}\,\text{M}^2$	$8{\cdot}1 \times 10^{-8}\,\text{M}^2$	$1{\cdot}0 \times 10^{-7}\,\text{M}^2$
(CaD)	$1{\cdot}3 \times 10^{-7}\,\text{M}^2$	$7{\cdot}8 \times 10^{-8}\,\text{M}^2$	

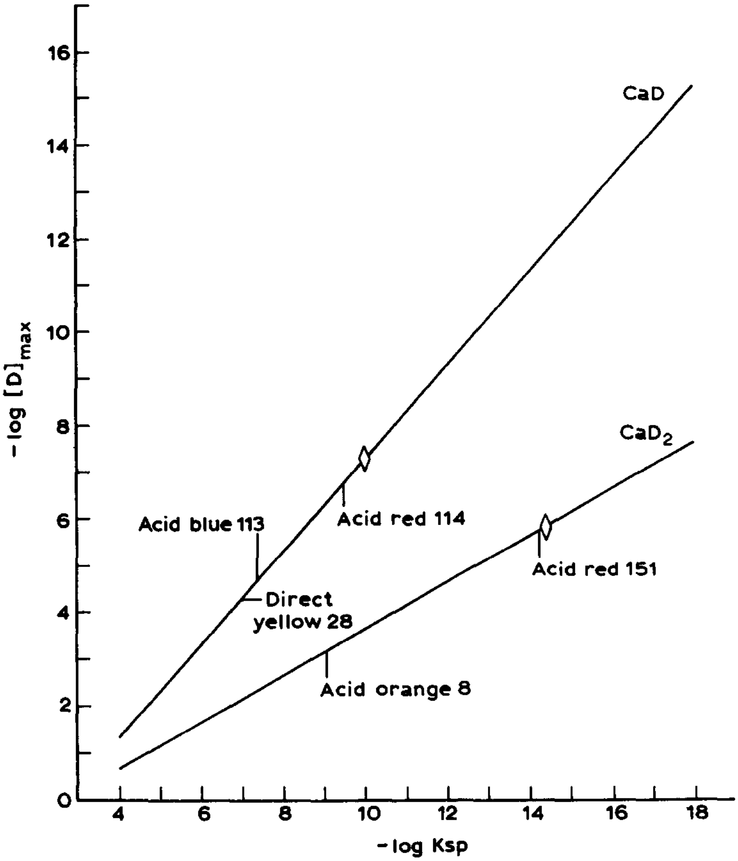

Fig. 1. Dye concentrations at Ca-salt precipitation.

mg/liter, respectively. It should be noted that any fixed K_{sp} and calcium concentration could also result in trivalent- and tetravalent-dye concentrations that are higher and a little lower, respectively, than the monovalent-dye concentration.

The above limiting values can be roughly compared with environmental concentrations of acid dyes reported by Tincher[14,15] for the Coosa River basin. The higher concentration $1{\cdot}4 \times 10^{-6}$ M (0·56 mg/liter) is only about three times as great as the highest concentration reported by Tincher.[14,15] The lower concentration 5×10^{-8} M (0·02 mg/liter), however, is well within the range he reported for several dyes.[14,15]

Acid Red 151 is the only dye from our study that was also reported on by Tincher.[14] In that case, his maximum concentration was about 1% of the solubility limit in 2×10^{-3} M Ca. The above considerations are based on extreme values and represent the worst case for Piedmont waters. Most of the STORET[12] values for Ca concentration were at least an order of magnitude less than the 0·002 M value used in this analysis. Even the Coosa River-basin waters (in a hard-water region) do not quite average 0·001 M Ca.[13] Thus, the concentration of acid and direct dyes will probably not be limited by precipitation unless large amounts of dye are discharged into a lake or stream. However, it should be noted that for hard waters as in the Coosa River system, several of Tincher's[14,15] reported values may have been at the solubility limit, since the dye solubilities are unknown.

Perhaps more importantly, the solubilities indicated above are, for hard waters, below the levels reported to be acutely toxic to fish.[21] This would not be the case for waters low in Ca. Little can be said regarding chronic toxicity levels in any case.

The utility and validity of these conclusions depend on whether the use and structures of dyes in this study are representative of those in use today. Regarding dye use, the AATCC Buyers' Guide for 1990[22] shows that all of the dyes studied are currently sold in the United States. The fact that most are made or sold by several companies suggests that they are widely used. Unfortunately, no data are available regarding the amounts of dyes that are used or discharged.

Whether the structures, and hence the solubility data, are representative is much less certain. For example, 49 of the 52 dyes in this study have structures in the Colour Index.[19] But, since newer dyes usually do not have structures in the public domain, it is impossible to say how closely they resemble the dyes in this study. The AATCC Buyers' Guide[22] shows that Colour Index structures are available for only about 55% and 69% of the direct and acid dyes, respectively. It is possible that more recent dyes, without Colour Index[19] constitution numbers, are more insoluble. The actual situation can only be determined when more data are available.

Perhaps the most important factor regarding the validity and use of the above data relates to pH effects. The results rely on the assumption that the dyes were studied in the least-soluble form. If this is not correct, then an environment having a different pH could result in a lower solubility. It seems far more likely, however, that different pH's in the environment would result in higher solubility.

5 CONCLUSIONS

Of the possible metal salts, the Ca salts of acid and direct dyes are most likely to precipitate after discharge to natural waters. However, many, if not most, of the dyes will not precipitate in even the hardest waters of the Southeastern Piedmont, unless dye concentrations exceed 0·02–0·6 mg/liter. Thus only in hard waters is dye solubility limited to levels below that required for acute fish toxicity. Such statements cannot be made confidently, in this regard, for soft waters or for dyes of unknown structure. This includes most of the Piedmont waters as well as the newer, and perhaps most widely used, dyes. Thus, important aspects of the fate of acid and direct dyes are likely to be determined by pathways other than precipitation.

The screening method is suggested as a simple and inexpensive method of determining whether anionic compounds will be removed from natural waters by precipitation.

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