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Experimental estimation of stability constants of copperised azo dyes in water

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Abstract

A simple spectrophotometric method is presented for estimation of pH-independent stability constants based on reaction of EDTA with copperised 1:1 azo dyes. Approximate stability constants for one direct and 11 fibre reactive dyes are presented. Examination of measurement precision and sources of error suggests the method to be accurate to within a factor of three.

Keywords: Equilibrium constant; Copperised dye; Fibre reactive dye

1. Introduction

The pH-independent stability constant is often used to assess the behavior of metal complexes. Consequently, many stability and other equilibrium constants have been measured for metal complexes of dyes because of their importance in analytical chemistry. Most often, equilibrium constants for such metal–ligand reactions are reported as conditional, i.e. concentration constants, rather than true thermodynamic values. Also, much of the published data is for non-aqueous solvents and cannot be reliably extrapolated to water.

Although the *o*–*o*′ copperised azo dyes comprise the largest group of copperised reactive dyes, we have been unable to find stability constants for any of these dyes. However, Jones [1] has pointed out that the stability constant for such dyes must be less than 10^{-15} mol/l. The reasons for this can be attributed primarily to difficulties in dye purification and unavailability of dye structures. Thus, when recent work on copperised azo dyes required a stability constant [2], it had to be estimated using data on copper complexes of only three dyes [3–5] and they were of a different dye class (mordant). The approach was justified on the assumption that copperised reactive and direct azo dyes have the same reaction centre as the copper complexes of the three mordant dyes and therefore would have similar stability constants. The stability constants for the mordant dye complexes ranged from $10^{-22.0}$ – $10^{-21.2}$. Of these dyes, only two are still listed in the AATCC buyer's guide [6].

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2. Approach

Accurate measurement of equilibrium constants utilises demanding laboratory techniques, highly purified chemicals and, increasingly, computerized data analysis. Thus, several books have been devoted to these topics [7–9]. However, many practical problems can be addressed using a reliable estimate of the constant. The following method depends on the use of visible spectrophotometry and the well-studied properties of EDTA and its copper complex.

The extent of dissociation, i.e. stability, of any 1:1 metal:ligand complex can be described by Eq. (1) and its associated pH-independent stability constant, Eq. (2). Here, CuL^{-n+2} is the colorant and L^{-n} is the colorant ligand. Charges are omitted from mathematical equations for simplicity.

$$\mathrm{CuL}^{-n+2} \rightleftharpoons \mathrm{Cu}^{+2} + \mathrm{L}^{-n} \tag{1}$$

$$K_\mathrm{S} = [\mathrm{Cu}][\mathrm{L}]/[\mathrm{CuL}] \tag{2}$$

Similarly, the reaction between EDTA, Y, and a copperised colorant anion can be written as the ligand exchange reaction in Eq. (3) and its equilibrium constant as Eq. (4).

$$\mathrm{CuL}^{-n+2} + \mathrm{Y}^{-4} \rightleftharpoons \mathrm{CuY}^{-2} + \mathrm{L}^{-n} \tag{3}$$

$$K = [\mathrm{CuY}][\mathrm{L}]\ /[\mathrm{CuL}][\mathrm{Y}] \tag{4}$$

The equation for dissociation of the Cu–EDTA complex, CuY, is given below in Eq. (5) and its stability constant in Eq. (6).

$$\mathrm{CuY}^{-2} \rightleftharpoons \mathrm{Cu}^{+2} + \mathrm{Y}^{-4} \tag{5}$$

$$K_Y = [\mathrm{Cu}][\mathrm{Y}]\ /[\mathrm{CuY}] = 10^{-18.8} \tag{6}$$

Multiplying Eq. (4) by Eq. (6) gives the pH independent stability constant of the dye, K_S, as a function of the concentrations of both EDTA and the Cu–EDTA complex, Eq. (7). Fortunately, metal–EDTA reactions are well studied and the stability constant for the copper complex is known [10].

$$K_S = K_\mathrm{Y} K = 10^{-18.8}[\mathrm{CuY}][\mathrm{L}]\ /[\mathrm{CuL}][\mathrm{Y}] \tag{7}$$

Since both [CuY] and [L] equal the difference between colorant concentrations before and after reaction with EDTA, Eq. (7) can be rewritten as shown in Eq. (8)

$$K_S = 10^{-18.8} K_\mathrm{Y} = 10^{-18.8}\frac{\left([\mathrm{CuL}]_\mathrm{O} - [\mathrm{CuL}]\right)^2}{[\mathrm{CuL}]\alpha_4\left([\mathrm{Y}]_\mathrm{O} - \left\{[\mathrm{CuL}]_\mathrm{O} - [\mathrm{CuL}]\right\}\right)} \tag{8}$$

Here, the initial colorant concentration is $[\mathrm{CuL}]_\mathrm{O}$ and [CuL] is its concentration after reaction with EDTA, $[\mathrm{Y}]_\mathrm{O}$ is the total concentration of EDTA before reaction and α_4 is the fraction of uncomplexed EDTA which is present as the quadrivalent anion. The pH variability of α_4 can be calculated using Eq. (9) [11].

$$\alpha_4 = \frac{10^{-21.09}}{10^{-4\mathrm{pH}} + 10^2(10^{-3\mathrm{pH}}) + 10^{-4.67}(10^{-2\mathrm{pH}}) + 10^{-10.83}(10^{-\mathrm{pH}}) + 10^{-21.09}} \tag{9}$$

The equilibrium concentration of colorant can be calculated from Eq. (10) where, for a given wavelength, a_meas is the measured absorbance and ε_C and ε_L are the extinction coefficients of colorant and colorant ligand, respectively.

$$[\mathrm{CuL}] = \left(a_\mathrm{meas} - \varepsilon_\mathrm{L}[\mathrm{CuL}]_\mathrm{O}\right)/(\varepsilon_\mathrm{C} - \varepsilon_\mathrm{L}) \tag{10}$$

Because both CuY and EDTA absorb visible light negligibly, the extinction coefficients for colorant and its ligand can be determined from solution spectra in the absence and presence of EDTA (excess Y^{-4}), respectively. The stability constant can then be calculated from Eq. (8).

Several requirements must be met in order to use this approach:

1. There must be enough difference between the visible spectra of colorant and ligand to provide measurable differences between the two extinction coefficients.
2. Hydrolysis of reactive or other functional groups on the colorant molecule must not significantly affect the difference between extinction coefficients.

3. If colorant stability is too great, the necessary EDTA concentration may be unattainable.
4. Reaction with EDTA must be fast enough to attain equilibrium before any competing reactions of colorant or ligand can become important.
5. pH of the system must be known at equilibrium.
6. Reaction of colorant with EDTA must not appreciably change the EDTA concentration, i.e. $\alpha_4[Y]_O >> [CuL]_O$.

3. Materials and methods

All dyes except one were supplied by the manufacturer as samples of commercial product. The exception was a sample of press cake. All colorants were 1:1 copperised azo molecules and were used as received. Except for one direct dye, all dyes were fibre reactive. For those dye structures not in the public domain, manufacturers provided the structure on the condition that it not be published.

Concentration of colorant in the commercial dyes and press cake was calculated from the copper content as determined, in duplicate, by inductively coupled plasma–mass spectrometry [12]. Resulting colorant content was found to vary from 22 to 78 wt.% except for one liquid dye. In that case the colorant content was lower, 8 wt.%.

Solvent was prepared to contain 0.010 M NaOH (pH 12.0) by weight in de-ionised water. Acid titration verified that the [OH] was accurate and stable to ±0.0005 M over the time of its use. This solvent was used to prepare stock solutions of commercial dye and of EDTA.

Dye solutions for spectrophotometry were prepared at concentrations of about 10–50 mg/l by dilution with solvent. This resulted in colorant concentrations on the order of 10^{-6}–10^{-5} M. Actual colorant concentration was dictated by the desire to keep concentrations low and to maintain absorbances in the range of about 0.5–1.5.

EDTA stock solution (0.01 M) was prepared by addition of reagent grade Na_4EDTA to the solvent. This stock solution was then added to the dye solutions to be used for spectrophotometry. For measurements, a set of five to six solutions were prepared, all of which had the same dye concentration but with EDTA varying from zero to about 0.01 M. Thus, the ratio of [EDTA] to $[CuL]_O$ increased to the point where the spectrum did not change on increasing [EDTA].

Under these conditions, spectra of solutions without EDTA provided extinction coefficients of the colorants, themselves. Solutions having the same colorant concentration but having $[EDTA] >> [CuL]_O$ gave a spectrum of the ligand at a known ligand concentration and hence, its extinction coefficient. The absorbance of intermediate solutions having a useful ratio of [EDTA] to [CuL] was used to calculate stability constants. After one set was measured, EDTA concentration could be optimized and the set size reduced.

Using the above solutions, the wavelength for absorbance measurement was found by subtracting the spectrum of the ligand from that of the colorant, the selected wavelength being that at which the difference between the spectra was maximal. Importantly, there often was a usable difference on each side of an isosbestic point. Thus, in some cases, two sets of calculations were made from a single set of spectra.

Absorption spectra were taken over the wavelength range of 400–700 nm using 1 cm fused silica cells and a computer controlled Shimadzu UV-2501PC spectrophotometer. Spectra were always obtained from two or more solution sets that differed in dye concentration at least by a factor of two. Spectra were stored in the computer for mathematical manipulation with Shimadzu spectrophotometer software [13].

Stability constants were calculated for each usable solution of a set and at each usable wavelength optimum in the wavelength range.

4. Results and discussion

Average values of the stability constants ranged from 4.5×10^{-22}–1.8×10^{-19}, Table 1. This is only a 400-fold range and supports the earlier assumption that different substituent groups on the dyes

Table 1
Equilibrium stability constants, K_S

Dye	K_S (mol/l)[a]	CV (%)[b]	N[c]	CI name
1	4.5E-22	54	12	
2	1.0E-19	15	5	Reactive Violet 5
3	3.8E-20	45	12	Reactive Violet 5
4	3.8E-20	57	9	
5	2.8E-21	54	11	
6	9.1E-21	32	10	Direct Blue 191
7	1.8E-19	22	8	Reactive Red 49
8	7.1E-21	17	8	Reactive Black 31
9	1.1E-20	37	18	Reactive Black 31
10	8.7E-21	57	8	
11	1.4E-20	35	18	Reactive Red 55
12	2.7E-21	52	11	

[a] Calculated from Eq. (8).
[b] Coefficient of variation.
[c] Number of calculations.

have a relatively small effect on the pH independent stability constants. Even the direct dye (dye no. 6) is in this range, as is the range for the mordant dyes (10^{-22}–$10^{-21.2}$) mentioned earlier.

The accuracy of the measurements cannot be evaluated from the presented data. However, the largest coefficients of variation are less than 60%, Table 1. Also, two of the dyes (Reactive Black 31 and Reactive Violet 5) were each present in two different commercial products. In both cases the stability constants agree within a factor of three. Therefore, it seems reasonable to conclude that the method can be used to estimate the pH independent stability constants with an accuracy of about a factor of three. Several aspects of the method that might be expected to influence the results are discussed below. Of these, kinetics is the most difficult to assess.

Several of the dyes had spectra suggestive of a poorly defined isosbestic point. This may result from EDTA–dye reactions that are slow compared to hydrolysis and/or structural changes due to hydrolysis. The deviations from an isosbestic point in these cases were small and experiments at different time intervals revealed only minor effects on the magnitude of the equilibrium constant. This is consistent with a small range of structural effects on both stability constants and spectra.

Accuracy and constancy of the pH is also critical since the fraction of EDTA present as the quadrivalent anion, α_4, is determined by pH. However, by working at pH 12 the system is effectively buffered. Also, it can be seen from Fig. 1 calculated from Eq. (9) that small changes in pH will have little effect on the value of α_4.

Finally, when a good estimate of the equilibrium constant is adequate, the method has the advantage of minimising some of the more common concerns. The usual problems with purity, volumetric accuracy and diluents in commercial dyes are likely to be small compared to the larger inherent sources of error mentioned above.

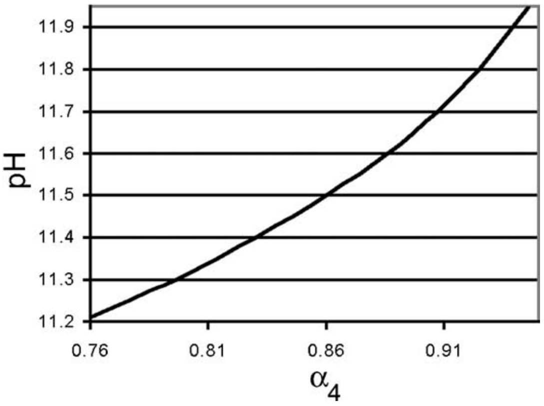

Fig. 1. Fraction of EDTA present as quadravalent anion, α_4, as a function of pH.

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