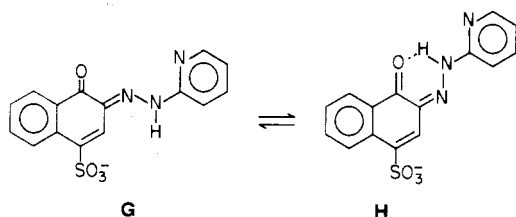


The undissociated form of dye 7 exists largely as the quinone hydrazone, and consideration of its geometries is instructive in view of its high reactivity. The nitrogen adjacent to the naphthalene ring becomes bonded to the metal ion in the 5-5 chelate, and conformation G is required ultimately for chelate formation.



The nitrogen with the attached proton is not involved. On the

other hand, conformation H results if the hydrazone is hydrogen bonded, and conversion to G requires the breaking of the bond coupled with isomerization. The high reactivity of the undissociated form of 7 suggests that the hydrogen-bonding possibility is not important with this dye.

The possibility of forming two 6-5 chelates may account for the slow equilibration in 1 after the initial chelation. If the less stable chelate forms more rapidly, the reequilibration to the more stable chelate would be slow because of the need to open and rearrange a tridentate chelate.

Acknowledgment. We are indebted to Professors D. W. Margerum and W. P. Jencks for helpful discussions of this work and to our Kodak colleagues for the dyes.

Registry No. 1, 94499-10-2; 2, 94499-11-3; Ni, 7440-02-0.

Contribution from the Research Laboratories and Kodak Park Division, Eastman Kodak Company, Rochester, New York 14650

Application of Factor Analysis to the Spectrophotometric Determination of Formation Constants of Complexes of Nickel(II) with Tridentate Dyes

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Absorption curves of solutions containing a dye ligand and its 1:1 and 1:2 nickel(II) complexes have been analyzed by factor analysis to extract the (often) inaccessible absorption curve of the 1:2 complex and its formation constant, K_2 . The method was applied to an *o,o'*-dihydroxy phenylazo dye, Solochrome Violet (SV), and to two α -[(2-hydroxyphenyl)azo]- α -acetoacetonitrile dyes. Required inputs are a family of absorption curves containing various proportions of the dye and two complexes, reference curves for the dye and the 1:1 complex, the pK_a 's of the ligand groups, and an independently determined value of the formation constant of the 1:1 complex, K_1 . The derived value of K_2 for SV agreed with the value determined earlier by potentiometric titration. The method was successful in cases where the absorption curves of the two complexes showed small differences in shape and/or λ_{max} but failed where the two curves differed only in amplitude. The values of K_1 and K_2 for the acetoacetonitrile dyes are smaller by several orders of magnitude than those of related dyes; the spectra and molecular models suggest that bond angles and lengths are distorted in the chelates. The advantages and disadvantages of the approach are discussed.

This paper describes a useful method for estimating formation constants of 1:2 complexes of metal ions and tridentate dye ligands from the spectra of three-component mixtures and its application to some dyes of interest in mechanistic studies.¹ Few constants for 1:2 complexes of such dyes have been reported. In appropriate applications the method has some advantages over other methods. The disadvantage of the potentiometric method in water is that the dyes are usually aggregated at concentrations where useful titrations can be made.^{2,3} The effort required to correct for the aggregation can be greater than that involved in measuring the stability constants.⁴ Spectrophotometric methods allow measurements at dye concentrations where aggregation is not a problem. The spectral methods have increased in sophistication from those that utilize absorbance changes at a single wavelength to computer-assisted regression and matrix methods that treat data at multiple wavelengths.⁵⁻¹⁰ The latter approach is highly desirable in the present application because the absorption curves of the 1:1 and 1:2 metal:dye complexes can be quite similar, and an equilibrium model that fits data at a single wavelength may fail when constrained to describe data at a number of wavelengths. Thus, the complexation of copper(II) with a bidentate azo dye is reported to give only two absorbing species¹¹ by application of the molar ratio,¹² Job's,¹³ straight line,¹⁴ and slope ratio¹⁵ methods to data at a given wavelength, whereas inspection of the complete absorption curves suggests that additional species are probably present.

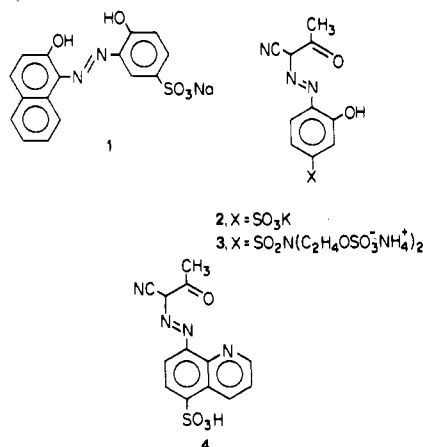
The application of factor analysis¹⁶⁻¹⁸ to a family of absorption curves made up of various contributions of components in equi-

librium utilizes all the information in the absorption curves and can, in principle, yield simultaneous estimates of an equilibrium constant and an unknown or inaccessible absorption curve. The successful application of the method of analysis to a study of the aggregation of azo dyes in water,³ where differences in the absorption curves of monomers, dimers, and *n*-mers are small, led us to try it with metal-dye complexation equilibria. In this paper we describe a study of the formation constants for the 1:1 (K_1)

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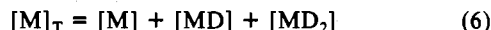
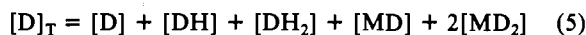
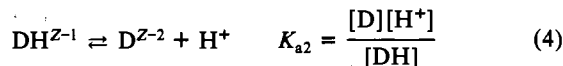
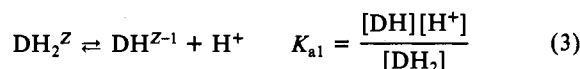
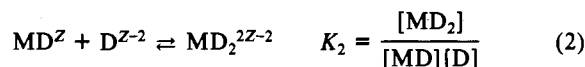
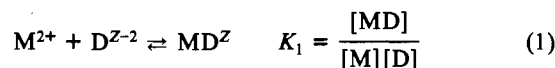
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and 1:2 (K_2) nickel(II):dye complexes of Solochrome Violet (SV) (1) and of three α -(aryloxy)- α -acetoacetonitrile dyes (2-4). A



spectrophotometric determination of K_1 and a potentiometric measurement of K_2 for SV have been reported⁴ and serve as a benchmark against which to evaluate our estimates. The complete absorption curves of each of the complexes have been determined in the visual region by direct measurement or by regression.

The chemical model of the dye-nickel system is defined by eq 1-6.¹⁹ By convention, M is hexaquaonickel, D is the dye species



with fully dissociated weak-acid ligands, and Z is the charge due only to the ligand groups and not the solubilizing groups. For convenience, the charge is omitted from the mass action and material balance equations. Equations 1-6 completely define the system, and if the equilibrium constants are known, the concentrations of all species can be calculated for any conditions of concentration or pH. The acid dissociation constants of the ligands of a particular dye usually differ sufficiently that only two of the three possible ionic species of uncomplexed dye need to be considered at a given pH, so that the system contains five unknown concentrations. Simultaneous solution of the five appropriate equations gives a cubic equation, the roots of which are evaluated by standard iterative methods.

Figure 1 shows sample calculations of concentration profiles for Solochrome Violet and its two complexes as a function of the molar ratio $[Ni]_T/[D]_T$ at two different pH values. The published values of the acid dissociation constants²¹ and the complex formation constants⁴ were used for the calculation. Since the ratio of ionic species of uncomplexed dye is fixed at a given pH, it was convenient to treat their sum as a single component in the plots.

Description of Method

A general description of the method and its application to another equilibrium study has been given.³ We will present only

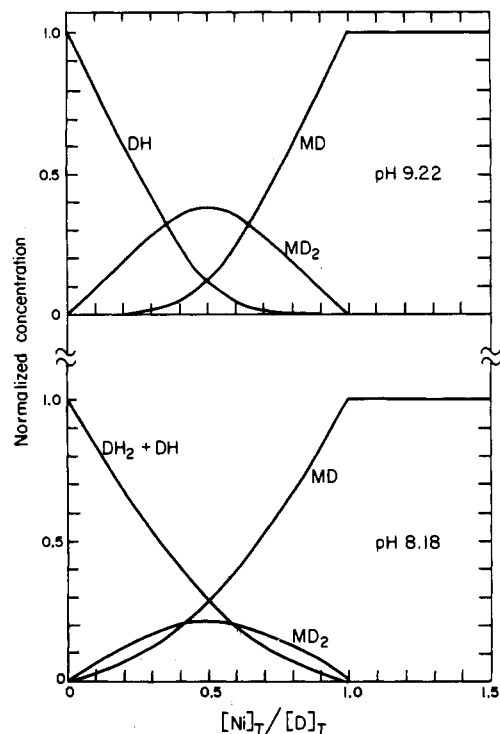


Figure 1. Concentration profiles of SV and its nickel(II) complexes as a function of the stoichiometric Ni:dye ratio, computed with the stability constants from ref 4. $[D]_T = 2.0 \times 10^{-5}$ M.

enough detail here to demonstrate its application to the equilibria of interest. In the present system the absorptivities of the unchelated nickel species are negligibly small compared to those of the dye species. A set of n absorption curves are obtained by successive additions of Ni(II) to a constant concentration of dye so that, in general, each curve may contain contributions from the three dye species, D, MD, and MD₂. If digital coordinates of the i th curve are read at p wavelengths, each $A_i(\lambda)$ can be represented by a $1 \times p$ vector. Any curve can be reconstructed at a given pH by

$$A_i = [DH]_i \epsilon_{DH} + [D]_i \epsilon_D + [MD]_i \epsilon_{MD} + [MD_2]_i \epsilon_{MD_2} \quad (7)$$

where A_i represents $A_i(\lambda)$ and the ϵ 's are $1 \times p$ vectors representing the $\epsilon(\lambda)$ for each component. The first two terms on the right-hand side behave as a single component at fixed pH so that mathematically, eq 7 represents a linear combination of three components:

$$A_i = [DH]_i (\epsilon_{DH} + K_{a2}[H^+]^{-1} \epsilon_D) + [MD]_i \epsilon_{MD} + [MD_2]_i \epsilon_{MD_2} \quad (8)$$

The set of n absorption curves are combined into an $n \times p$ data matrix:

$$A = \begin{bmatrix} A_1(\lambda_1) & \dots & A_1(\lambda_p) \\ \vdots & \dots & \vdots \\ A_n(\lambda_1) & \dots & A_n(\lambda_p) \end{bmatrix} \quad (9)$$

The three largest eigenvectors of the second moment matrix, M , are derived, where $M = [A'A]/n$ and A' is the transpose of A . If eq 8 is correct, the entire set of A_i can be reconstructed, within error, by a linear combination of the three eigenvectors:

$$A_i = \alpha_{1i} V_1 + \alpha_{2i} V_2 + \alpha_{3i} V_3 \quad (10)$$

It can be shown that the ϵ 's of the pure species must be also be linear combinations of the same eigenvectors:

$$\epsilon_{App} = \eta_{11} V_1 + \eta_{12} V_2 + \eta_{13} V_3 \quad (11)$$

$$\epsilon_{MD} = \eta_{21} V_1 + \eta_{22} V_2 + \eta_{23} V_3 \quad (12)$$

$$\epsilon_{MD_2} = \eta_{31} V_1 + \eta_{32} V_2 + \eta_{33} V_3 \quad (13)$$

(19) We retain the earlier convention²⁰ of designating the stoichiometries of the complexes by MD and MD₂ and reserve the conventional symbol L for individual ligand groups within the dye.

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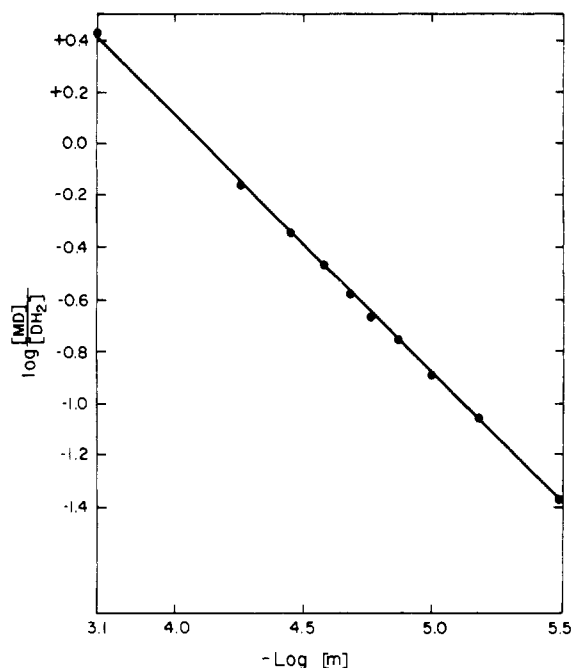


Figure 2. Plot for determining K_{eq} for dye 2 from eq 20 (pH 4.69 acetate buffer, 25 °C, $I = 0.01$ M, $[\text{OAc}^-] = 0.01$ M).

where $\epsilon_{\text{App}} = \epsilon_{\text{DH}} + K_{\text{a2}}[\text{H}^+]^{-1}\epsilon_{\text{D}}$. The ϵ 's are evaluated by evaluating the vector coefficients η_{ij} .

Substituting eq 11–13 into eq 8, collecting the coefficients of V_1 , V_2 , and V_3 , and equating the resulting coefficients to those in eq 10 give

$$\alpha_{1i} = [\text{DH}]\eta_{11} + [\text{MD}]\eta_{21} + [\text{MD}_2]\eta_{31} \quad (14)$$

$$\alpha_{2i} = [\text{DH}]\eta_{12} + [\text{MD}]\eta_{22} + [\text{MD}_2]\eta_{32} \quad (15)$$

$$\alpha_{3i} = [\text{DH}]\eta_{13} + [\text{MD}]\eta_{23} + [\text{MD}_2]\eta_{33} \quad (16)$$

Equations 14–16 give the relationships between the derived vector coefficients required to reproduce any measured absorption curve in the data set (the α 's), the coefficients required to reproduce the curves of the pure components, and the concentrations of the components. The latter are fixed by the equilibrium constants of the eq 1–4 and the material balance relationships.

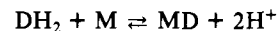
The first three eigenvectors accounted for 100% of the variability above noise in absorbance matrices from curves containing contributions from three absorbing components. The variability in reduced sets of two absorbing components was accounted for fully by two eigenvectors. Determination of the minimum number of eigenvectors needed to account for the variability above noise is equivalent to determining the rank of the absorbance matrix.

In the system under study, the acid dissociation constants of the weakly acidic ligands are determined independently by conventional methods. The ϵ_{App} is obtained from the absorption curve of dye at the pH of the experiment in the absence of Ni(II). The ϵ_{MD} is obtained from the dye curve measured in an excess of Ni(II). In the present systems, K_1 was larger than K_2 by at least 2 orders of magnitude so that a fivefold excess of Ni(II) over the 1:1 stoichiometric amount was sufficient to convert all the dye to the 1:1 complex. The ϵ_{MD_2} is often inaccessible by direct measurement since the other species coexist with MD_2 at the 1:2 Ni:dye stoichiometric ratio under most conditions (Figure 1). In principle, the MD_2 complex becomes the exclusive species at this ratio at sufficiently high pH.

If $K_1 > K_2$, the concentration of MD_2 decreases with decreasing pH relative to that of MD (Figure 1) until at some pH its contribution becomes negligible and K_1 can be measured directly by application of simple spectrophotometry^{4,22} to the two-component

system (see below). The derived value of K_1 is entered as a fixed parameter for the estimation of K_2 by regression on the three-component system at higher pH. If the ϵ 's are all sufficiently different, factor analysis can estimate ϵ_{MD} , and K_2 simultaneously from the same data set. In the system under study, however, ϵ_{MD} and ϵ_{MD_2} are too similar so that unique values of ϵ_{MD_2} and K_2 could not be obtained by estimating them simultaneously. The curve shape ϵ_{MD_2} was determined by factor analysis in a separate experiment at a higher pH and then used as a fixed parameter for estimating K_2 from data at the lower pH.

Determination of K_1 . In dilute acetate buffers (pH 4.5–5.2) complexation is incomplete, and the only two absorbing species were DH_2 and MD. We define an equilibrium in terms of DH_2 :



$$K_{\text{eq}} = \frac{[\text{MD}][\text{H}^+]^2}{[\text{DH}_2][\text{M}]} = K_1 K_{\text{a1}} K_{\text{a2}} \quad (17)$$

$$[\text{D}]_{\text{T}} = [\text{DH}_2] + [\text{DH}] + [\text{MD}] = \gamma[\text{DH}_2] + [\text{MD}] \quad (18)$$

where $\gamma = 1 + K_{\text{a1}}/[\text{H}^+]$ and corrects for any dye present as DH. Let α (the degree of complexing) = $(A_{\text{D}} - A)/A_{\text{MD}}$, where A_{D} and A_{MD} are the absorbances of dye and 1:1 complex, respectively, at some wavelength, and A is the absorbance of a mixture. Then

$$[\text{MD}] = \alpha[\text{D}]_{\text{T}} \quad [\text{M}] = [\text{M}]_{\text{T}} - \alpha[\text{D}]_{\text{T}}$$

and

$$[\text{DH}_2] + [\text{DH}] = (1 - \alpha)[\text{D}]_{\text{T}} \quad [\text{DH}_2] = \frac{(1 - \alpha)[\text{D}]_{\text{T}}}{\gamma}$$

Substituting into eq 17 gives

$$K_{\text{eq}} = \frac{\alpha[\text{H}^+]^2}{\left(\frac{1 - \alpha}{\gamma}\right)([\text{M}]_{\text{T}} - \alpha[\text{D}]_{\text{T}})} \quad (19)$$

Values of K_{eq} are calculated from eq 19 at various nickel concentrations to verify the constancy of the computed K 's. Alternatively, $\log K_{\text{eq}}$ values can be obtained graphically by using eq 17 in logarithmic form:

$$\log K_{\text{eq}} = \log \left(\frac{[\text{MD}]}{[\text{DH}_2]} \right) + 2 \log [\text{H}^+] - \log [\text{M}] \quad (20)$$

A plot of $\log ([\text{MD}]/[\text{DH}_2])$ vs. $-\log [\text{M}]$ is linear with unit slope. At the point where $\log ([\text{MD}]/[\text{DH}_2])$ is zero, $-\log [\text{M}] = \log K_{\text{eq}} + 2(\text{pH})$. An example is shown in Figure 2. K_1 is obtained from K_{eq} by using eq 17 and the values of K_{a1} and K_{a2} measured independently.

If $K_1 \approx K_2$, the situation just described does not apply. We have shown by computer simulation and by experiment²⁰ that when the two constants are similar, decreasing the pH decreases the degree of complexing but does not change the ratio of complexes appreciably. A spectral titration by the molar ratio method gives the ratio of the two constants but not individual values.²⁰

Absorption Curve and Formation Constant of the 1:2 Complex. Figure 1 shows that if $K_1 > K_2$, there will be some pH at which dye and MD_2 are the only absorbing species present at low molar ratios ($R = [\text{Ni}]_{\text{T}}/[\text{D}]_{\text{T}}$). At this pH and with tridentate dyes, all the nickel added is quantitatively converted to complex so that the concentrations of dye and complex are known from the stoichiometry. A series of approximately six absorption curves measured at R values in the range $0 < R < 0.3$ provides data from which ϵ_{MD_2} in eq 8 is estimated by regression, using either factor analysis or some other appropriate computer-assisted method.²³ The estimated ϵ_{MD_2} is then entered as a fixed parameter into the program for subsequent determination of K_2 .

(22) This is not true if $K_1 \approx K_2$; in this case values of the individual constants cannot be obtained by the present method.²⁰

(23) Metzler, D. E.; Harris, C. M.; Reeves, R. L.; Lawton, W. H.; Maggio, M. S. *Anal. Chem.* 1977, 49, 864A.

The pH at which the contribution from MD is negligible at low R values is found empirically. The presence of sharp isosbestic points for part of the data set from the nickel titration establishes the presence of only two of the three absorbing components. Since ϵ_{MD} and ϵ_{MD_2} are usually similar, precision spectrophotometry and rigid criteria for the existence of isosbestic points are necessary.

K_2 is estimated by factor analysis either from the complete set of curves at the pH where ϵ_{MD_2} was estimated or, preferably, from a complete data set measured at a lower pH where all three absorbing components contribute to the A_i over the entire range of the titration (Figure 1). Our program allows us the option of fixing any of the K 's or ϵ 's or allowing them to vary as adjustable parameters. For evaluating K_2 , all the ϵ 's and all the K 's except K_2 were fixed. Initial estimates of K_2 for the regression were made by considered guesses, based on the values of K_1 .

Experimental Section

The sample of Solochrome Violet was described earlier.³ Dyes 2-4 were synthesized in house and were gifts. Inorganic salts were removed from 2 by dissolving the dye in dry DMF, filtering, and concentrating the filtrate. The recovered dye was recrystallized twice from a mixture of deionized water and ethanol. A small amount of EDTA was added in the first recrystallization. Elemental analyses for C, H, N, and S agreed with calculated values for $C_{10}H_8N_3KO_2S \cdot 2H_2O$ to within 0.1%. Dye 3 gave a satisfactory elemental analysis and a single band on a chromatogram and was used as received. Dye 4 was converted from a mixed salt to the sulfonic acid by precipitation from base by acidification with hydrochloric acid. Field desorption mass spectrometry gave only the parent peak for the acid. Elemental analyses for C, H, N, and S agreed with calculated values for $C_{13}H_{10}N_4O_4S \cdot H_2O$ to within 0.2%. Kodak reagent grade tris(hydroxymethyl)aminomethane (Tris) was treated with decolorizing carbon in water, the filtered solution was evaporated, and the residue was recrystallized twice from ethanol containing a little deionized water. The ethanol had been distilled in an all-glass still. A small quantity of EDTA was added with the first recrystallization.

All glassware used in the study was soaked initially in 0.1% EDTA solution overnight. Subsequent cleanings utilized detergent and thorough rinsings with ammonia solutions followed by distilled water.

Stock solutions of Ni(II) (0.1 M) were prepared as the sulfate or the chloride and were standardized against Acculute standard EDTA solutions by using pyrocatechol violet as end-point indicator. Separate solutions were prepared volumetrically for each R ratio. Aliquots of the Ni(II) stock solutions were delivered by a Gilmont micrometer buret.

Absorption curves were measured on a Cary 118C recording spectrophotometer with calibrated optical glass cells. Wavelength and photometric accuracy were checked before and during the study. Digital absorbance data were obtained and processed as described before.³ The factor analysis was done on an IBM 370 computer with the MODSAC-3 program. The total residual error for solution preparation and spectrophotometry was 0.00325 absorbance unit.³

Acid dissociation constants were determined spectrophotometrically at $I = 0.04$ M in buffered solutions containing 1 mM EDTA. pK_{a1} values were measured in maleic acid or MES¹ buffers and pK_{a2} values were measured in carbonate or HEPPS¹ buffers.

Results

The method is very sensitive to small perturbations in the absorption curves so that it was essential to maintain constant pH for each solution in the nickel titration. The useful pH range for estimating K_2 (7-9) required the use of buffers. Some solutions of metalizable dyes and nickel required overnight equilibration to attain constant absorption curves,^{1,20} and colloidal suspensions of insoluble complexes would often form during the equilibration if zwitterion buffers²⁴ that do not complex nickel^{20,24} were used. The problem of solubility was avoided by using Tris buffer, which does form complexes with nickel(II)²⁵ according to equilibria 21-23. The increased solubility may be due in part to the for-

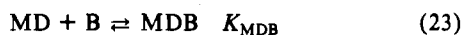
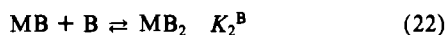
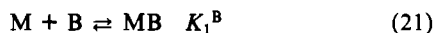


Table I. Spectral Parameters for the 1:1 and 1:2 Complexes of the Dyes in Aqueous Solution

dye	MD		MD ₂	
	λ , nm	$10^{-4} \epsilon$	λ , nm	$10^{-4} \epsilon^a$
1	520	2.29	513	2.02
			538	2.03
2	441	1.86	447	1.70
			438	1.61
3	440	1.90	447	2.45
			447	2.45

^a Absorptivity per mole of dye in the complex. The absorptivity per mole of complex would be twice these values.

mation of the ternary complexes (eq 23). We measured K_{MDB} for Solochrome Violet and Tris by spectrophotometry and obtained a value of 175 M^{-1} . Because of the additional ligation equilibria in Tris buffers, the measured formation constant for the 1:2 nickel:dye complex is defined by eq 24. The difference between

$$K_2' = \frac{[MD_2]}{[D]([MD] + [MDB])} = K_2 \left(\frac{1}{1 + K_{MDB}[B]} \right) \quad (24)$$

K_2 and K_2' should be small for most purposes at the concentration of Tris used here (0.01 M). Our value for K_{MDB} for nickel-Tris-SV gives $K_2 = 2.8K_2'$ for SV.

Values of K_1 were obtained directly in dilute acetate buffers ([acetate ion] = 0.01 M) since complexation of Ni(II) with acetate is negligible at the levels of nickel used.²⁶ K_1 for SV was measured earlier by spectrophotometry in an acetate buffer⁴ and was not redetermined. Titration of solutions of dyes 2 and 3 in acetate buffer to a fivefold excess of Ni(II) gave families of curves with excellent isosbestic points at 408 and 405 nm, respectively. Complexation equilibrium was not attained for several hours so the solutions were equilibrated overnight at 25 °C before measurement. Values of K_{eq} calculated by eq 19 were constant at various degrees of complexing. Plots prepared according to eq 20 were linear with the theoretical slope (Figure 2).

Spectral titration of dye 4 by the molar ratio and pH variation methods gave responses similar to those for α -PAN dyes²⁰ and indicated that K_1 and K_2 had similar values. Analysis of the spectral changes by the method described earlier²⁰ gave $K_1/K_2 = 2.4$ with a standard deviation of 0.4.

The absorption curve of the 1:2 complex of 4 was measured directly at $R = 0.5$ at pH 9.2. The curves for the same complexes of SV and dyes 2 and 3 were estimated by factor analysis in Tris buffers at pH 9.22, 7.87, and 7.86, respectively. At these pH values, the observed curves gave sharp isosbestic points in the titration range of $0 < R < 0.3$. Six curves measured at various R values within this range, the reference curve, ϵ_D , and the material balance relationships $[MD_2] = [Ni]_T$ and $[D] = [D]_T - 2[Ni]_T$ permitted ϵ_{MD_2} to be estimated by factor analysis. Two eigenvectors described all the variability in the experimental curves taken over the limited range (absorbance matrix of rank 2). Absorption curves corresponding to the original R values were reconstructed by using the measured ϵ_D , the estimated ϵ_{MD_2} , and the derived eigenvectors. The total residual standard error for reconstruction of all curves at more than 50 wavelengths was within experimental error.

The absorption curves of the dye and the two complexes of 1, 2, and 4 are shown in Figures 3-5. The corresponding curves of 3 are similar to those of 2. The curves of MD₂ are plotted as absorptivity per mole of dye in the complex rather than as ϵ per mole of complex in order to duplicate the relative amplitudes of the curves observed during a titration. As such, the ϵ for MD₂ in the figures are half the ϵ_{MD_2} used in the computations (eq 8). The spectral parameters of the two complexes of each dye are summarized in Table I.

Values of K_2' were usually estimated at a lower pH than that at which ϵ_{MD_2} was estimated to ensure that the three absorbing

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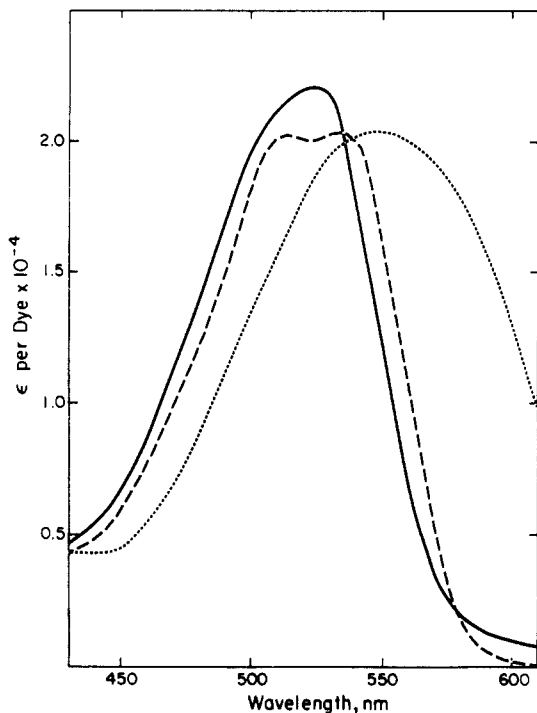


Figure 3. Absorption curves of SV (···) and its 1:1 (—) and 1:2 (---) nickel complexes. The curves of the dye and the 1:1 complex were measured; that of the 1:2 complex was derived by factor analysis (pH 8.18 Tris buffer, 25 °C).

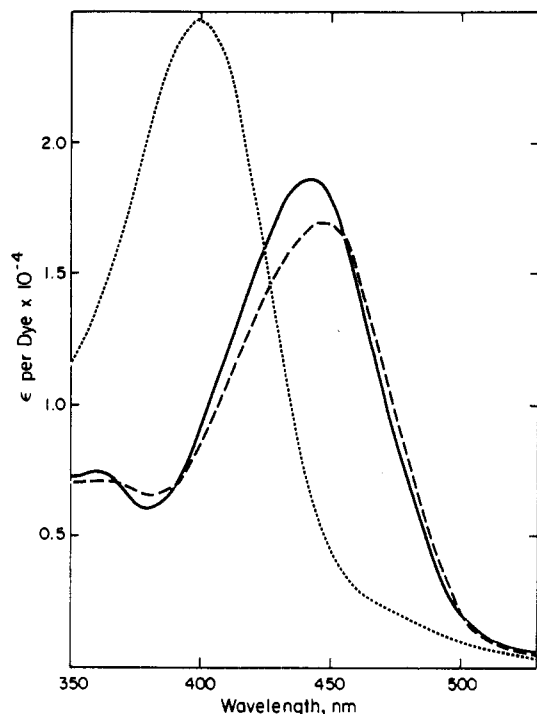


Figure 4. Absorption curves of dye 2 (···) and its 1:1 (—) and 1:2 (---) nickel complexes. The curves of the dye and the 1:1 complex were measured; that of the 1:2 complex was derived by factor analysis (pH 8.77 Tris buffer, 25 °C).

components would coexist over the whole titration. The absorbance matrix for the titration was of rank 3. In addition to the digital experimental curves, the input data included K_{a1} , K_{a2} , K_1 , ϵ_D , ϵ_{MD} , and ϵ_{MD_2} . The ϵ_{MD_2} that had been determined separately by regression was merged with the new data set by use of a file management program.

Table II summarizes the values of the various equilibrium constants determined in this study along with the pH at which

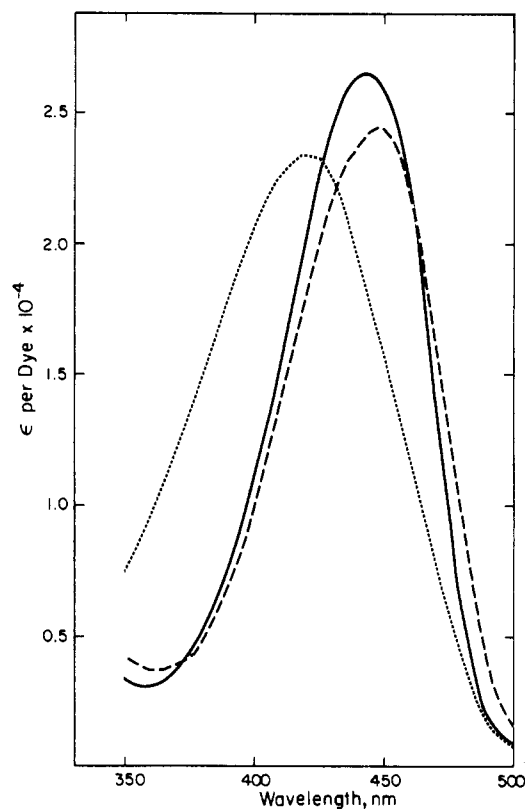


Figure 5. Absorption curves of dye 4 (···) and its 1:1 (—) and 1:2 (---) nickel complexes. All curves were measured directly (pH 9.22 Tris buffer, 25 °C).

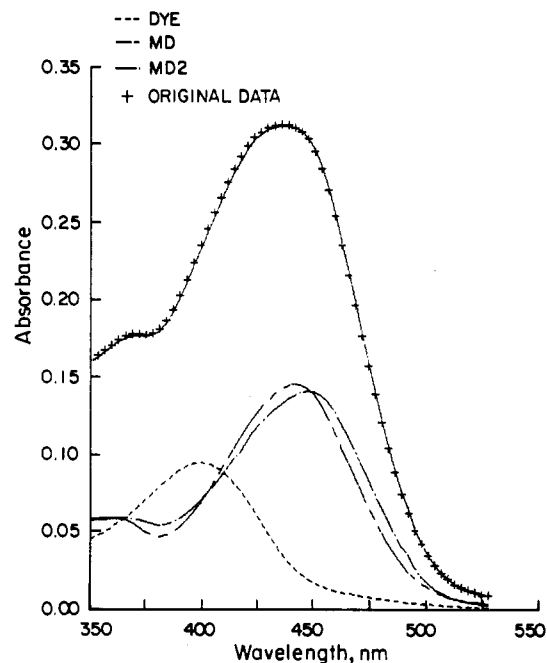


Figure 6. Reconstruction of the absorption curve of dye 2 at an R ratio of 0.6 (pH 7.19), using ϵ_{MD_2} and the K_2' value determined by factor analysis.

K_2' was determined and the estimated standard deviation for K_2' .

Absorption curves corresponding to each nickel concentration in the titration were computed via eq 8 by using the estimated values of K_2' and the other fixed constants and ϵ 's. A typical reconstruction for dye 3 is shown in Figure 6. The continuous curve through the data points was computed by summing the contributions of the three components that were calculated by the model. The total residual standard error for reconstruction of

Table II. Formation Constants of Nickel-Dye Complexes and Dissociation Constants of the Dyes at 25 °C^a

dye	pK _{a1}	pK _{a2}	K ₁ , M ⁻¹	K ₂ , M ⁻¹	K ₂ ', M ⁻¹	s, ^b M ⁻¹	pH of detmn
1	7.24 ^c	13.4 ^c	1.0 × 10 ¹⁶ ^d	2.5 × 10 ¹⁰ ^d (1.2 × 10 ¹¹) ^e	5.6 × 10 ¹⁰	0.5 × 10 ¹⁰	8.18
2	6.11	10.14	1.3 × 10 ¹¹		1.3 × 10 ⁸	0.03 × 10 ⁸	7.19
3	5.80	9.38	3.2 × 10 ¹⁰		7.2 × 10 ⁷	1.0 × 10 ⁷	7.86
4		7.31	K ₁ /K ₂ = 2.4		8.4 × 10 ⁷	1.0 × 10 ⁷	7.17

^a I = 0.04 M in the present work. ^b Estimated standard error in K₂' from the regression. ^c Reference 21. ^d Reference 4. ^e Calculated from K₂' via eq 24.

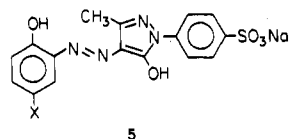
all curves in all sets was within the experimental error of 0.003 25 absorbance unit except for dye 3 where the residuals were 0.004 17 absorbance unit.

Discussion

The application of factor analysis to the determination of stability constants of dye complexes has some advantages over other spectrophotometric methods. The method retains all the information in an absorption curve and permits the curve to be described simply by a linear combination of the products of several eigenvectors and associated eigenvalues. By requiring a model to fit a data set at all wavelengths, one increases the sensitivity, the confidence in the model, and the precision of the estimated parameters. Sensitivity is important in cases such as the present one where differences in curve shape between two of several absorbing components is small.

To our knowledge, others have apparently not observed or been aware that the initial products obtained by titrating a dye with nickel may give kinetically controlled product mixtures^{1,20} and that long equilibration times may be needed to obtain thermodynamically controlled product mixtures. Methods that do not allow for the required equilibrations when needed will give questionable results.

The use of factor analysis is not appropriate when K₁ and K₂ have similar values, as with 4 and with some α-PAN dyes.²⁰ Titration by the molar ratio method gives two sets of two-component absorption curves²⁰ from which the K's can be estimated more simply by other methods. Factor analysis of absorbance matrices also fails to yield unique values of K₂ from absorption curves of solutions containing the three chemical components if the shapes of the curves of two of the components are too similar. We attempted to apply the method to spectral data for a series of pyrazolone dyes of general structure 5 and their nickel(II)



complexes. The regressions for estimating K₂ failed to converge because the shapes of the curves of MD and MD₂ were too similar. A typical example of curves of the complexes of 5 (X = SO₂CH₃) is shown in Figure 7. Although the curves for the two complexes differ in amplitude, there is no difference in the absorption maximum and very little difference in shape. In the limit where the shapes are identical, ε_{MD} and ε_{MD₂} would differ only by a constant amplitude factor δ and eq 8 reduces to

$$A_i = [\text{DH}]\epsilon_{\text{App}} + ([\text{MD}]_i + \delta[\text{MD}_2]_i)\epsilon_{\text{MD}} \quad (25)$$

where ε_{MD₂} = δε_{MD}. In this event the system is underdetermined and it becomes impossible to know how much of a change in absorption curve is due to MD or MD₂. Differences in curve shape as small as those shown in Figure 4 are sufficient for resolution when the complete absorption curves are used.

Our value of log K₂ for SV is 11.1 after correction of K₂' via eq 24, compared to the value of 10.4 obtained by pH titration.⁴ Table II shows that the estimated standard errors for K₂' from the regression program are 14% of the regression values or less. To determine how sensitive the method is to errors in K₂', error curves were generated by computer simulation. All parameters

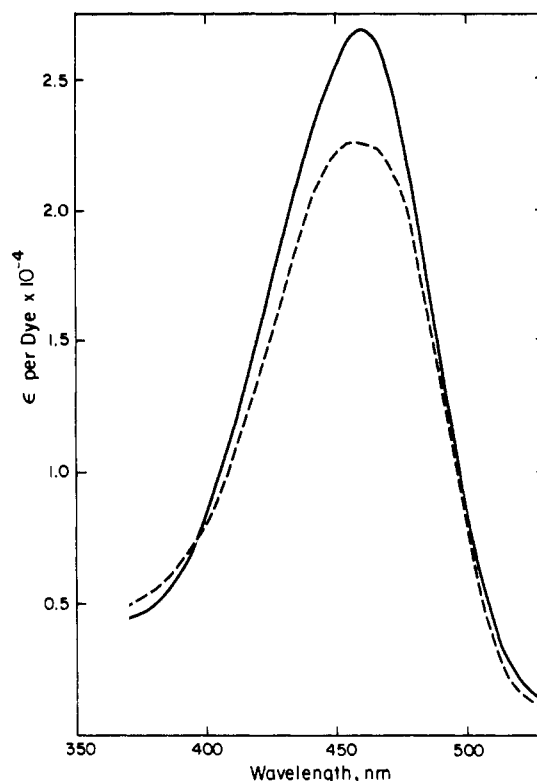


Figure 7. Absorption curves of the 1:1 (—) and 1:2 (---) nickel complexes of the (aryloxy)pyrazolone dye 5 (X = SO₂CH₃). The curves were measured or derived from data (pH 8.18 Tris buffer).

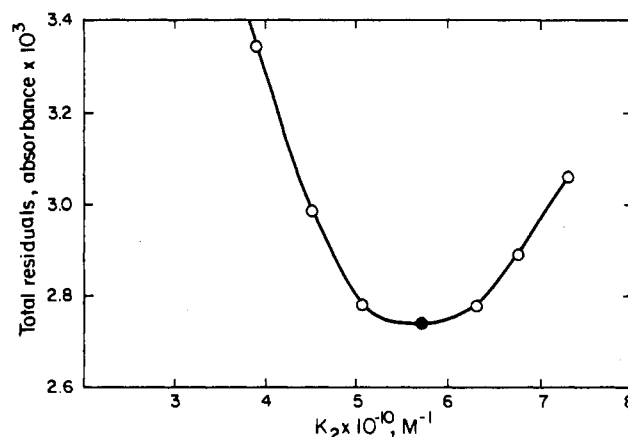


Figure 8. Plot of the total residual error for reconstructing 11 absorption curves of SV with simulated errors of ±10, ±20, and ±30% of the regression value. The filled data point is the regression value.

for SV were fixed. Values of K₂' were fixed at ±10, ±20, and ±30% of the regression value. Figure 8 shows the residuals for reconstructing the original absorption curves when K₂' was varied as indicated. The error curve is sensitive to small errors in K₂', and the regression value falls in a shallow minimum. An error of ±20%, however, would give a residual that is within the estimated experimental error.

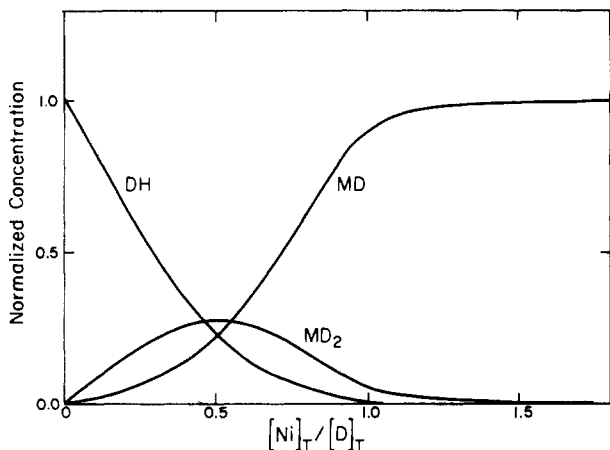


Figure 9. Concentration profiles of dye 3 and its nickel(II) complexes as a function of the R ratio. $[D]_T = 8.0 \times 10^{-6}$ M.

The formation constants for 2 and 3 are smaller than those for SV by several orders of magnitude. The K_1 values of 2 and 3 are also smaller than those of several (arylamino)pyrazolones²⁷ (5) by the same amount. Since all the chelates contain one six- and one five-membered ring and the same ligand atoms are involved in all cases, the lower values of K_f for 2 and 3 probably result from steric effects. Space-filling models of 2-4 show steric crowding of the ligand groups in coplanar conformations needed to form the chelates and suggest that bond angles and distances may be distorted in the complexes of these dyes. Table I and Figures 4 and 5 show that the complexes of 2-4 have maximum absorbance

(27) Unpublished results.

at nearly the same wavelength but that the absorptivities of the complexes of 2 and 3 are about 30% lower than those of 4. This suggests that the dye moieties in the chelates of 2 and 3 are twisted slightly out of coplanarity²⁸ compared to dye 4.

Although a number of K_1 values have been published for complexes of metal ions with *o,o'*-dihydroxy azo dyes,²⁹ there are few published examples of both K_1 and K_2 for the same metal-dye system. The results of Coates and Rigg⁴ on SV show that $K_2 < K_1$ by several orders of magnitude for a number of metal ions. Our results for dyes 2 and 3 show that $K_2' < K_1$ by factors of 400 and 1000, respectively. The effect of reducing the difference between the constants on the composition of a system as a function of the molar ratio is seen by comparing Figures 1 and 9. Figure 9 shows the calculated fractions of the various species of 3 as R is varied. The comparison shows that as the difference between the K 's decreases, the symmetry in the profiles about the R ratio of 0.5 decreases and larger excesses of the metal ion are required to completely convert all the dye to the 1:1 complex. A very few data suggest that the replacement of a 2-hydroxyaryl moiety by a 2-pyridyl or an 8-quinolyl moiety decreases the difference in the K 's until they are essentially the same.^{20,30} In this situation, all symmetry in the molar ratio titrations is lost.²⁰ As the values of the two K 's become more similar, the 1:2 complex becomes increasingly predominant at $R = 0.5$, and a larger excess of metal ion is required for complete conversion to the 1:1 complex.

Registry No. 2, 94519-58-1; 3, 94519-59-2; 4, 94519-60-5.

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Reaction of the Tetrahydroxoargentate(III) Ion with Thiosulfate

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The reaction of $\text{Ag}(\text{OH})_4^-$ with thiosulfate ion (T), potentially an eight-electron reductant, was studied over the range 2.5×10^{-6} M $\leq [\text{T}] \leq 0.2$ M in 0.6 M NaOH. At lowest [T], reaction via the aquated silver(III) species, $\text{Ag}(\text{OH})_3\text{H}_2\text{O}$, results in a monothiosulfato complex, $\text{Ag}(\text{OH})_2\text{S}_2\text{O}_3^{2-}$, which undergoes internal redox with a rate constant of 0.22 ± 0.03 s⁻¹. The stability constant of the complex is about $(1.4 \pm 0.2) \times 10^4$ and an absorption maximum for the species occurs at 260 ± 5 nm. At $[\text{T}] > 1.0 \times 10^{-3}$ M, Ag(III) is reduced by T without hydroxyl replacement. The rate law contains four terms with first- and second-order contributions predominating at high [T]: $-\text{d}[\text{Ag}(\text{III})]/\text{d}t \sim (D[\text{T}] + E[\text{T}]^2)[\text{Ag}(\text{III})]$. At 25 °C and $\mu = 1.2$ M, $D = 158 \pm 30$ M⁻¹ s⁻¹ and $E = 768 \pm 94$ M⁻² s⁻¹. The presence of a third-order term is attributed to the reaction of T with a five-coordinate Ag(III)-T species. The principal product at excess T is tetrathionate.

Introduction

The tetrahydroxoargentate(III) ion, $\text{Ag}(\text{OH})_4^-$, is a strongly oxidizing square-planar system that can be prepared by the electrochemical oxidation of a silver anode in 1.2 M NaOH.^{1,2} The complex is metastable in this medium, decomposing at room temperature with a half-life of approximately 1.5 h.

The hydroxyl ion is a strongly σ -donating ligand in square-planar complexes and, consequently, a poor leaving group in ligand-substitution reactions.^{3,4} This increase charge reduction on the metal and partly explains the ability of the hydroxyl group

to stabilize the +3 oxidation state of silver. Reductions of silver(III) by potential ligands can occur simultaneously with hydroxyl replacement or within a five-coordinate intermediate.^{5,6} In some cases, displacement of hydroxyl by, for example, azide⁷ and tetraglycine⁸ has resulted in the formation of novel silver(III) complexes.

The decomposition of the monoazido Ag(III) complex to silver(I) and nitrogen requires the participation of a second N_3^- as in other transition-metal oxidations of this ion.⁹ A similar pattern is observed in the oxidations of thiosulfate by transition metals that, like Ag(III), act as two-electron oxidants.^{10,11}

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