Spectrophotometric Determination of Complex Formation Constants Between a New Schiff Base and Some Transition Metals by Rank Annihilation Factor Analysis

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Rank annihilation factor analysis (RAFA) was used for the spectrophotometric studies of complex formation between a new Schiff base derived from 3,6-bis((aminoethyl)thio)pyridazine and some transition metals in dimethylformamide (DMF). Formation constants of these complexes were derived using RAFA on spectrophotometric data. According to molar ratio data and Job's plot, the stoichiometry of complexation between the Schiff base and the Ni^{2+}, Co^{2+}, Cu^{2+}, and Zn^{2+} cations was 1:1 and for Pd^{2+} was 2:1. The logarithm of the complex formation constants was found to be 5.66 for Ni^{2+}, 5.1 for Co^{2+}, 7.08 for Cu^{2+}, 6.73 for Zn^{2+}, and 7.77 for Pd^{2+}.

Introduction

Schiff bases are ligands with a variety of donor atoms exhibiting interesting coordination modes toward various metals.[1−3] Several reports have been published on the investigation of their photochromic and thermochromic properties,[4] proton transfer tautomeric equilibria,[5] biological and pharmacological activities,[6−9] as well as their suitability for analytical applications.[10,11]

Stability constants can be key parameters for the investigation of equilibria in solution. They are very important in many fields such as industrial chemistry,[12] environmental studies,[13] and medicinal[14] and analytical chemistry.[15] Therefore, complexation reactions of metal ions with different ligands have been widely studied.[16−18] Several methods for the determination of stability constants, such as potentiometric titration,[19] conductometry,[20] and spectrophotometric determination,[21] have been reported. Among the methods used for the determination of stability constants, spectrophotometric methods have the advantage of sensitivity and are suitable for determination of stability constants in solution under different experimental conditions. Overlapping of spectra of different chemical species involved in the equilibria is an important problem because it makes the determination of stability constants by classical methods difficult or even impossible and can cause great uncertainties on the obtained results. This problem can be easily overcome using chemometric methods,[22,23] where one can analyze whole spectra, thereby utilizing all spectral information.

Rank annihilation factor analysis (RAFA) was originally developed by Ho et al. as an iterative procedure.[24] It was modified by Lorber to yield a direct solution of a standard eigenvalue problem[25] and can be employed to quantitatively analyze gray systems with an unknown background. RAFA has been used in different fields including spectrophotometric study of chemical kinetics,[26,27] spectrophotometric determination of acid dissociation constants, and the formation constants of metal−ligand complexation.[28−30]

In this article, we used RAFA for the determination of the stability constants of some transition metal ions with the recently synthesized Schiff base (3,6-bis((2-aminoethyl-5-Br-salicyliden)thio)pyridazine, PABST).

Theory. The basis of the application of RAFA in the spectrophotometric determination of stability constants was described in a previously published work.[31] A two-way data matrix with rank 2 can be formed by measuring absorbance spectra for a constant concentration of the desired compound at different metal−ligand molar ratios. The concentration profiles are calculated by optimizing the value of the stability constants, and the rank of the original data matrix reduces by one by removing the information related to the ligand in the matrix.

For a 1:1 complex formation between a metal ion, M, and a ligand, L

$$\mathrm{M} + \mathrm{L} \rightleftharpoons \mathrm{ML} \tag{1}$$

the stability constant is

$$K_\mathrm{f} = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]} \tag{2}$$

where [L], [M], and [ML] are the equilibrium concentrations of ligand, metal ion, and the complex, respectively. The mass balances of the system can be written as

$$C_\mathrm{L} = [\mathrm{L}] + [\mathrm{ML}] \tag{3}$$

$$C_\mathrm{M} = [\mathrm{M}] + [\mathrm{ML}] \tag{4}$$

where C_L is the total concentration of ligand, which remains constant, and C_M is the total concentration of metal ion, which is varied when employing the molar ratio method. At zero molar ratio, the recorded spectrum is the spectrum of the pure ligand. Substitution of [M] and [ML] from eqs 3 and 4 into eq 2 and rearranging yields

$$K_\mathrm{f}[\mathrm{L}]^2 + (K_\mathrm{f}C_\mathrm{M} - K_\mathrm{f}C_\mathrm{L})[\mathrm{L}] + [\mathrm{L}] - C_\mathrm{L} = 0 \tag{5}$$

The equilibrium concentration of free ligand can easily be obtained from the roots of eq 5 by knowing the values of C_M,

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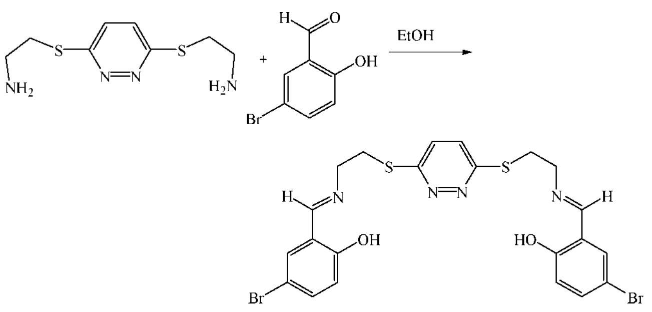
Scheme 1



C_L, and K_f. The equilibrium concentrations of the metal and complex can be obtained from the following equations

$$[ML] = C_L - [L] \tag{6}$$

$$[M] = C_M - [ML] \tag{7}$$

A two-way data matrix with rank 2 can be formed by measuring absorbance under different wavelengths at a series of metal to ligand molar ratios with constant analytical concentrations of the ligand. By removing the contribution of one component from the original absorption data matrix using RAFA, the rank of the residual matrix decreases by one. By substitution of different values of K_f in eq 5 for a given amount of C_M and C_L, different vectors of ligand concentration will be obtained. The correct concentration profile will be obtained by substitution of the correct K_f value. The molar absorptivity of the ligand can be obtained from the spectrum of the pure ligand. Therefore, the correct absorption spectra for the ligand at different metal−ligand molar ratios is obtained by multiplying the concentration profile of the ligand by its molar absorptivity. By removing the ligand spectra from the original absorption data matrix, the rank of the residual matrix reduces by one.

On the basis of principal component analysis (PCA), the RSD (Relative Standard Deviation) method is widely used to determine the number of principal components.[32,33] The RSD is a measure of the lack of fit of a principal component model to a data set. The RSD is defined as

$$\mathrm{RSD}(n) = \left(\frac{\sum_{i=n+1}^{c} g_i}{n(c-1)} \right)^{1/2} \tag{8}$$

where g_i is the eigenvalue; n is the number of considered principle components; and c is the number of samples.

For a 2:1 metal−ligand molar ratio complex, the equations are as follows

$$2M + L \rightarrow M_2L \tag{9}$$

$$K_f = \frac{[M_2L]}{[L][M]^2} \tag{10}$$

$$C_L = [L] + [M_2L] \tag{11}$$

$$C_M = [M] + 2[M_2L] \tag{12}$$

By substitution of [M] and [ML] from eqs 11 and 12 into eq 10 and rearranging yields

$$4K_f[L]^3 + K_f(4C_M - 8C_L)[L]^2 + K_f(4C_L{}^2 + C_M{}^2 - 4C_MC_L)[L] + [L] - C_L = 0 \tag{13}$$

If the values of C_M, C_L, and K_f are known, it is possible to obtain the free ligand concentration [L] from the roots of the associated polynomial. The equilibrium concentration of the remaining species can be easily calculated from eqs 11 and 12. The correct K_f value will be obtained by using RAFA.

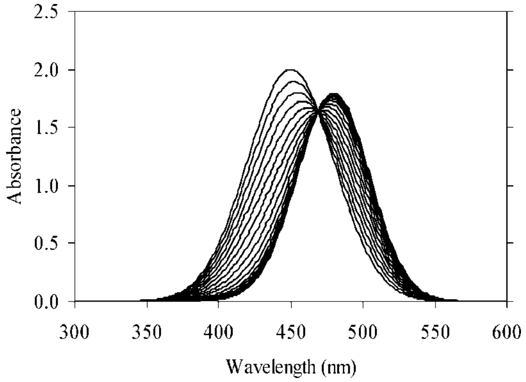


Figure 1. Simulated absorption spectra of a 1:1 metal−ligand complex formation system at a fixed concentration of ligand and various concentrations of metal ions. log $K_f = 4.74$, $\lambda_{max}(L) = 450$ nm, $\lambda_{max}(ML) = 480$ nm.

Table 1. Results of PCA on Simulated Data

i	g_i	$g_i/g_i + 1$	RSD
1	2530.4	9.94000	7.130
2	254.60	530416	0.013
3	0.00048	1.11000	0.009
4	0.00043	1.07500	0.006
5	0.00040	1.08000	0.003
6	0.00037		

Experimental

Apparatus and Materials. Absorption spectra were obtained with a Perkin-Elmer Lambda 45 UV−vis spectrophotometer using 1 cm path length glass cells, and the measurements were performed at (27 ± 0.1) °C. All experiments were performed with analytical reagent grade chemicals purchased from Merck (Darmstadt, Germany) and used without further purification. The Schiff base was synthesized in the laboratory. DMF, *n*-hexane, methanol, ethanol, 3-bromo-6-hydroxy benzaldehyde, chloride salts of Ni^{2+}, Cu^{2+}, Co^{2+}, and Pd^{2+}, and the nitrate salt of Zn^{2+} were used. All solutions were prepared fresh daily. All calculations were performed in MATLAB 6.5 (Math Works, Cochituate Place, MA) and Microsoft Excel 2003.

Preparation of 3,6-Bis((2-aminoethyl-5-Br-salicyliden) thio) Pyridazine (PABST). PABST was synthesized from 3,6-bis((aminoethyl)thio)pyridazine (PTA). PTA was prepared as described previously[34] and used for preparation of PABST as follows (Scheme 1). A solution of 3,6-bis((aminoethyl)thio)pyridazine (PTA) (1 mmol) in absolute EtOH (10 mL) was added to a stirring solution of 3-bromo-6-hydroxy benzaldehyde (2 mmol) in absolute EtOH at 50 °C over a period of 10 min. The solution was heated in a water bath for 2 h at 70 °C with stirring. The obtained yellow solid was filtered off, washed with cooled *n*-hexane/ethanol (2/1), and dried in air. Overall Yield: 80%, m.p. = (177 to 179) °C. ^{1}H NMR (d_6-DMSO, RT, ppm): δ 3.58 (t, 4H), 3.93 (t, 4H), 6.83 (d, 2H), 7.44 (d, 2H, $J = 2.40$ Hz), 7.47 (s, 2H), 7.66 (d, 2H, $J = 2.40$ Hz), 8.55 (s, 2H), 13.14 (br, 2H). ^{13}C(^{1}H)NMR (d_6-DMSO, RT, ppm): δ 166.1, 160.4, 158.5, 135.3, 133.4, 126.6, 120.7, 119.5, 109.6, 57.7, 30.6. IR (KBr, cm^{-1}): 1634(C=N), 1604, 1570, 1479, 1443(C=C), 1385, 1362, 1271(C−O), 1150, 826.

Procedure. Stock solutions of Schiff base and metal ion salts were prepared in DMF. The analytical ligand concentration was kept constant, and different concentrations of metal ions were added to the ligand solution. Then, after 1 h the spectrum of

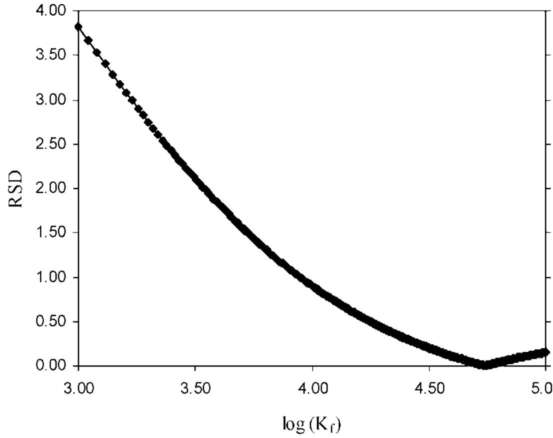


Figure 2. Relationship between RSD and stability constant, K_f, 1:1 complexation system obtained log (K_f) = 4.74.

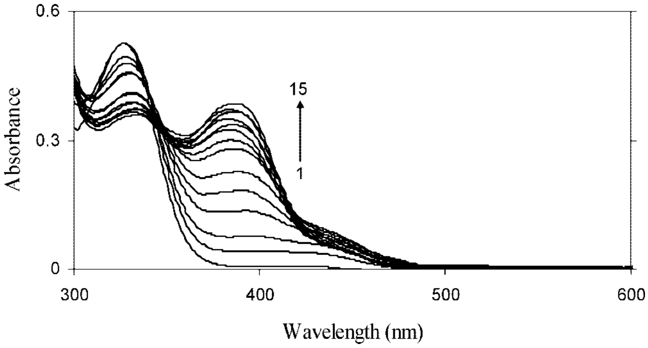


Figure 3. Experimental absorption spectra for the Ni^{2+} complex with Schiff base. The analytical concentration of Schiff base is $8 \cdot 10^{-5}$ ($mol \cdot L^{-1}$) with different concentrations of metal in the range of 0.0 to 2.2 molar ratio of metal to ligand. The concentrations of metal is: 1, 0.0; 2, $8 \cdot 10^{-6}$; 3, $1.6 \cdot 10^{-5}$; 4, $2.4 \cdot 10^{-5}$; 5, $3.2 \cdot 10^{-5}$; 6, $4 \cdot 10^{-5}$; 7, $5.6 \cdot 10^{-5}$; 8, $6.4 \cdot 10^{-5}$; 9, $8 \cdot 10^{-5}$; 10, $9.6 \cdot 10^{-5}$; 11, $1.12 \cdot 10^{-4}$; 12, $1.28 \cdot 10^{-4}$; 13, $1.44 \cdot 10^{-4}$; 14, $1.6 \cdot 10^{-4}$; and 15, $1.76 \cdot 10^{-4}$ ($mol \cdot L^{-1}$).

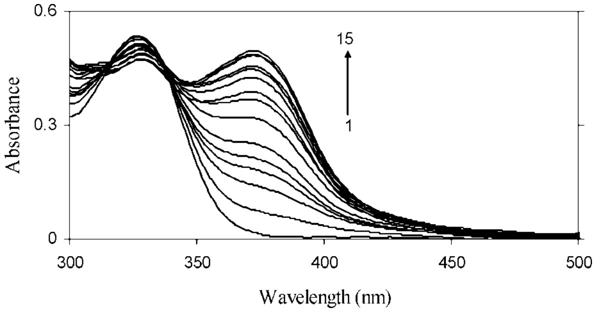


Figure 4. Experimental absorption spectra for the Co^{2+} complex with Schiff base. The concentration of ligand and metal ion is the same as described in Figure 3.

solution was obtained between (300 and 800) nm in 1 nm intervals. The molar ratio method was used to determine the stoichiometry of the metal−ligand complex, and the RAFA program was used to calculate the complex formation constant. All specific details are given in the next section.

Results and Discussion

Simulated Data. Figure 1 shows the created absorption spectra for a 1:1 metal−ligand complex formation system at a fixed concentration of ligand and various concentrations of metal ion.

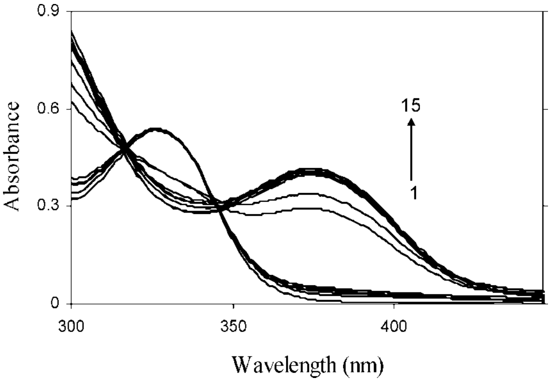


Figure 5. Experimental absorption spectra for the Cu^{2+} complex with Schiff base. The concentration of ligand and metal ion is the same as described in Figure 3.

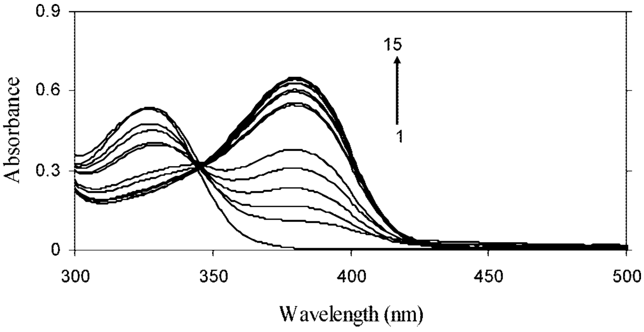


Figure 6. Experimental absorption spectra for the Zn^{2+} complex with Schiff base. The concentration of ligand and metal ion is the same as described in Figure 3.

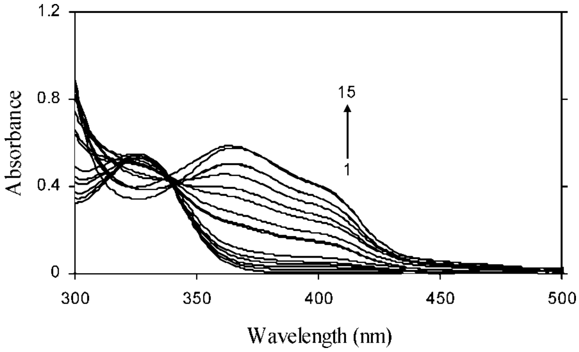


Figure 7. Experimental absorption spectra for the Pd^{2+} complex with Schiff base. The concentration of ligand and metal ion is the same as described in Figure 3.

Table 1 presents the eigenvalues, ratios of consecutive eigenvalues, and RSD of the simulated matrix. The synthetic data matrix was processed by the RAFA method, and the relationship between the RSD of the residual matrix and the stability constant (K_f) is shown in Figure 2. A minimum is observed in the RSD curve shown in Figure 2 which indicates the optimum value of log K_f. The applied noise was ± 0.1 % absorbance units.

As seen in Table 1, the ratio of two consecutive eigenvalues is too large at the second eigenvalue, so there are two principle components (absorptive species) in the simulated matrix. This method was also used to determine the number of principle components in the experimental absorbance matrices.

The program was tested for different complex formation constants with different noise levels. The results for simulated data showed that the predicted K_f values and the obtained absorption spectra and concentration profiles are in good agreement with the selected ones.

Real data. Figures 3 to 7 show the experimental absorption spectra for the complex between the investigated Schiff base

Table 2. Results of PCA on Experimental Data

	g_i					$g_i/(g_i + 1)$					RSD				
i	Ni	Co	Cu	Zn	Pd	Ni	Co	Cu	Zn	Pd	Ni	Co	Cu	Zn	Pd
1	111.10	218	199.19	195.25	256.27	16.55	25.34	11.55	9.01	11.97	1.07	1.19	1.69	19	19
2	6.70	8.60	17.25	21.70	21.41	43.34	765.6	311.3	864.4	58.86	0.12	0.033	0.071	0.047	0.17
3	0.15	0.011	0.055	0.025	0.36	18.31	7.74	11.17	12.58	34.06	0.023	0.011	0.017	0.011	0.028
4	0.008	0.0015	0.005	0.002	0.010	6.40	2.35	38.54	8.79	3.46	0.008	0.006	0.003	0.004	0.012
5	0.001	0.0006	0.00013	0.0002	0.003	5.43	1.84	1.56	2.84	9.14	0.003	0.004	0.002	0.002	0.004
6	0.0002	0.0003	0.00008	0.00008	0.0003	2.17	7.17	1.19	1.46	1.99	0.002	0.001	0.001	0.001	0.002
7	0.0001	0.00005	0.00007	0.00005	0.0002										

and Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, and Pd^{2+}, respectively, when the ligand concentration is constant and the metal concentration is varied. The molar ratio data for the investigated complexes showed a 1:1 metal to ligand stoichiometry for the Ni^{2+}, Co^{2+}, Cu^{2+}, and Zn^{2+} complexes. The molar ratio data and Job's plot showed a 2:1 metal to ligand stoichiometry for the palladium complex. The maximum wavelength of the ligand was observed at 330 nm. The maximum wavelengths of complexes were observed at 387 nm, 375 nm, 375 nm, 382 nm, and 364 nm for Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, and Pd^{2+}, respectively.

The number of absorptive species may also be determined by applying PCA on the data matrix shown in Figures 3 to 7. Table 2 shows the PCA results on the experimental data. There are two principle components (absorptive species including ligand and one type of complex) for complexation of Co^{2+} with the Schiff base. The same procedure was performed for other cations, and two absorptive species were also found for the Ni^{2+}, Cu^{2+}, Zn^{2+}, and Pd^{2+} systems. The absorption spectrum for the Pd^{2+} complex seems to show two maxima, but the PCA results and also Job's plot did not show more than one type of complex. The RAFA program was performed on experimental absorbance data matrices in the range of 0.0 to 2.2 metal−ligand molar ratios.

The value of the stability constant for each complex was optimized by the proposed method. The relationship between RSD and K_f for cobalt experimental data after processing RAFA on the absorption matrix is shown in Figure 8. Table 3 shows the estimated complex formation constants for the investigated metal−Schiff base complexes.

The data in Table 3 show that the sequence of stability constants of Schiff base complexes with the cations of the first transition series (i.e., $Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$) follows the Irving−Williams order,[35] which generally holds for the equilibrium constants of transition metals.

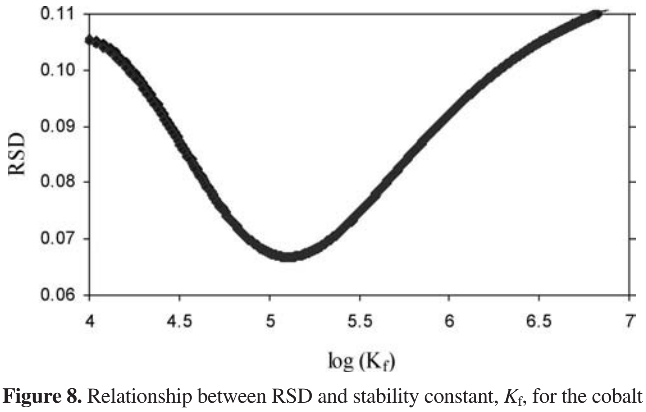


Figure 8. Relationship between RSD and stability constant, K_f, for the cobalt complex.

Table 3. Results of K_f for Metal−Schiff Base Complexes[a]

complex	Ni−L	Co−L	Cu−L	Zn−L	Pd−L
log K_f	5.66 ± 0.01	5.10 ± 0.02	7.08 ± 0.01	6.73 ± 0.004	7.77 ± 0.01

[a] L, Schiff base.

Conclusions

RAFA is proposed as an efficient chemometric algorithm for the complete analysis of complex formation systems by the spectrophotometric molar ratio method. The RAFA is based on the principle that the rank of a two-way bilinear matrix of pure compounds is one. The proposed method makes it possible to obtain the stability constants, pure absorption spectra, and species concentration profiles in several ligand−metal complex formation systems when there is severe spectral overlapping.

The method was tested with simulated data sets, and reliability was obtained by reproducing the input formation constants and species concentration profiles. The method was also applied to experimental data in 1:1 and 2:1 metal−ligand complex formation. The investigated Schiff base forms 1:1 complexes with Ni^{2+}, Co^{2+}, Cu^{2+}, and Zn^{2+} and a 2:1 complex with Pd^{2+} in DMF.

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