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Application of Rank Annihilation Factor Analysis to the Spectrophotometric Determination of the Formation Constants of Complexes of a New Schiff Base and Some Transition Metals in Different Media

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The complex formation between a new synthesized Schiff base and the cations Ni^{2+}, Co^{2+}, Cu^{2+}, and Zn^{2+} in ethanol, dimethylformamide (DMF), and acetonitrile (AN) was studied spectrophotometrically using rank annihilation factor analysis (RAFA). According to molar ratio data and Job's plots, the stoichiometry of complexation between the Schiff base and the cations Co^{2+}, Ni^{2+}, and Zn^{2+} was 1:2, and that between the Schiff base and Cu^{2+} in all solvents and Zn^{2+} in AN was 1:1. Formation constants of these complexes were derived using RAFA on spectrophotometric data. In this process the contribution of the ligand is removed from the absorbance data matrix when the complex stability constant acts as an optimizing object, and simply combined with the pure spectrum of ligand, the rank of the original data matrix can be reduced by one by annihilating the information of the ligand from the original data matrix. Also the effect of surfactants such as sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), and Triton X-100 on the complex formation constant of Cu^{2+} with the Schiff base in DMF was investigated.

Introduction

Schiff bases have often been used as chelating ligands in the field of coordination chemistry, and their metal complexes are of great interest. It is well-known that N and S atoms play a key role in the coordination of metals at the active sites of numerous metallobiomolecules.[1] Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer, and herbicidal applications.[2] Chelating ligands containing N, S, and O donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions.[3] It is known that the existence of metal ions bonded to biologically active compounds may enhance their activities.[4,5]

Stability constants can be key parameters for the investigation of equilibria in solution. They are very important in many fields such as industrial chemistry,[6] environmental studies,[7] and medicinal[8] and analytical chemistry.[9] Therefore, complexation reactions of metal ions with different ligands have been widely studied.[10−12] Several methods for the determination of stability constants, such as potentiometric titration,[13] conductometry,[14] and spectrophotometric determination,[15] have been reported. Among the methods used for the determination of stability constants, spectrophotometric methods have the advantage of sensitivity and are suitable for the 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 in the obtained results. There are some classic programs used in the multiwavelength spectrophotometric determination of stability constants such as LETAGROP-SPEFO[16] or SQUAD.[17] Chemometric methods can also easily resolve the overlapped spectra,[18,19] 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.[20] It was modified by Lorber to yield a direct solution of a standard eigenvalue problem[21] and can be employed to quantitatively analyze gray systems with an unknown background. RAFA has been used in different fields including the spectrophotometric study of chemical kinetics and[22,23] spectrophotometric determination of acid dissociation constants and the formation constants of metal−ligand complexation.[24−27] In the present work we used RAFA for the determination of the stability constants of some transition metal ions with a recently synthesized Schiff base in different solvents. Also, the effect of surfactants on the stability constant of Cu^{2+} with the Schiff base in DMF was investigated.

Theory

The basis of the application of RAFA in the determination of the formation constants for 1:1 complexes was described in our previous work.[25]

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

$$M + L \rightarrow ML \qquad (1)$$

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$$K_f = \frac{[ML]}{[M][L]} \tag{2}$$

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

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

where [L], [M], and [ML] are the equilibrium concentrations of ligand, metal ion, and the complex, respectively. K_f is the stability constant of the complex, 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.

Substitution of [M] and [ML] from eqs 3 and 4 into eq 2 and rearranging yield

$$K_f[L]^2 + (K_fC_M - K_fC_L)[L] + [L] - C_L = 0 \tag{5}$$

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

$$M + 2L \rightarrow ML_2 \tag{6}$$

$$K_f = \frac{[ML_2]}{[L]^2[M]} \tag{7}$$

$$C_L = [L] + 2[ML_2] \tag{8}$$

$$C_M = [M] + [ML_2] \tag{9}$$

where [L], [M], and [ML_2] are the equilibrium concentrations of ligand, metal ion, and the complex, respectively. K_f is the stability constant of the complex, 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.

Substitution of [M] and [ML_2] from eqs 8 and 9 into eq 7 and rearranging yield

$$K_f[L]^3 + (2K_fC_M - K_fC_L)[L]^2 + [L] - C_L = 0 \tag{10}$$

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 8 and 9. The correct K_f value will be obtained by using RAFA.

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 10 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 are 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.[28,29] The RSD is a measure of the lack of fit of a principal component model to a data set. The RSD is defined as:

$$\mathrm{RSD}(n) = \left(\frac{\sum_{i=n+1}^{c} g_i}{n(c-1)}\right)^{1/2} \tag{11}$$

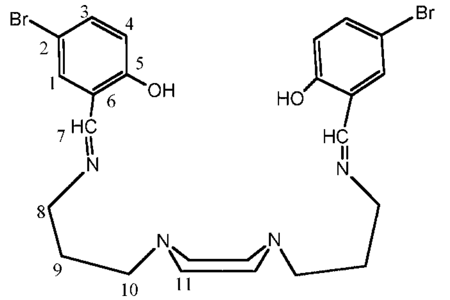
where g_i is the eigenvalue, n is the number of considered principal components, and c is the number of samples. The RSD was used as a formula to obtain the optimum stability constant. In an iterative procedure, different stability constants are put in eq 10, and different concentration profiles of ligand are obtained. The contribution of ligand is removed from the absorbance data matrix (with rank 2) for each obtained concentration profile of ligand, and then according to the RSD equation (eq 11), the sum of eigenvalues of the residual matrix is obtained from eigenvalue 2 to c (number of samples). If the rank of the residual matrix is reduced by one, the sum of eigenvalues from eigenvalue 2 to c will equal the noise level, and the minimum RSD is obtained. So by scanning K_f values and estimating RSD per each K_f, the optimum stability constant will be obtained when RSD has its lowest value.

Experimental Section

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 (25 ± 0.1) °C. All experiments were performed with analytical reagent grade chemicals. The Schiff base was synthesized in the laboratory. Dimethylformamide (DMF), acetonitrile (AN), ethanol, diethyl ether, sodium sulfate, 5-bromosalicylaldehyde, silica gel, sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), Triton X-100, chloride salts of Ni^{2+}, Cu^{2+}, Co^{2+}, and Zn^{2+}, and nitrate salt of Ni^{2+} were purchased from Merck (Darmstadt, Germany), and *N*,*N*′-bis(3-aminopropyl)piperazine was supplied from Aldrich and used without further purification. All solutions were prepared fresh daily. All calculations were performed in MATLAB 6.5 (Math Works, Cochituate Place, MA) and Microsoft Excel 2003.

General Procedure for the Synthesis of Schiff Base ((Z)-2-((3-(4-(3-(5-Bromo-2-hydroxybenzylideneamino)propyl)piperazin-1-yl)propylimino)methyl)-4-bromophenol) (PBHP). 5-Bromosalicylaldehyde (1 mmol, 0.201 g), *N*,*N*′-bis(3-aminopropyl)-piperazine (0.5 mmol, 0.1 g), and silica gel (0.5 g) were mixed together in a tube and irradiated in a microwave oven. The progress of the reaction was monitored by gas chromatography. Upon completion of the reaction, the crude product was recrystallized from ethanol and then dried over sodium sulfate. The solvent was evaporated, and the product was washed with diethyl ether and dried. The product was identified by melting point, mass spectrum, elemental analysis, and IR and ^{1}H and ^{13}C NMR spectra. Anal. Calc. for $C_{24}H_{30}Br_2N_4O_2$ (MW: 566.33): C, 50.90; H, 5.34; N, 9.89. Found: C, 50.92; H, 5.30; N, 9.90 %. Yield: 0.25 g (88 %). mp (107.0 to 109.0) °C. IR (Nujol, cm^{-1}): 1635 [υ(C=N)], 1163(s) [υ(C−O)]. MS (EI): $m/z = 566$ [Schiff base]$^+$. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δH: 1.81 (m,

Scheme 1. Structure of the Synthesized Schiff Base



4H, 9-H), 2.33−2.40 (m, 12H, 10-H, and 11-H), 3.58 (t, ^3J = 8.0 Hz, 4H, 8-H), 6.79−7.31 (m, 6H, aromatic ring), 8.20 (s, 2H, 7-H, −C=N), 13.49 (bs, 2H, −OH). ^{13}C NMR (400 MHz, $CDCl_3$, ppm) δC: 27.8 (t, C-9), 53.2 (t, C-11), 55.8 (t, C-10), 57.4 (t, C-8), 109.8 (s, C-6), 119.1 (d, C-5), 120.1 (s, C-2), 153.2, 154.8 (d, C-3 or C-4), 160.5 (s, C-5) (aromatic ring), 163.8 (d, C-7, −C=N).[30] Scheme 1 shows the structure of the synthesized Schiff base.

Experimental Procedure. Stock solutions of PBHP and metal ion salts were prepared in ethanol, DMF, and AN. The analytical ligand concentration was kept constant, and different concentrations of metal ions were added to the PBHP solution. Then after 30 min the spectrum of the solution was obtained between (300 to 800) nm in 1 nm intervals. The molar ratio data and Job's plots were used to determine the stoichiometry of the metal−ligand complexes, and the RAFA program was used to calculate the complex formation constant. All specific details are given in the next section.

Results and Discussion

Figure 1 shows the experimental absorption spectra for the complexes between PBHP and Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} in ethanol, when the ligand concentration is constant and the metal concentration is varied. The molar ratio data and Job's plot for the investigated complexes showed a 1:2 metal-to-ligand stoichiometry for the Co^{2+}, Ni^{2+}, and Zn^{2+} complexes and a 1:1 metal-to-ligand stoichiometry for the Cu^{2+} complex. Job's plots are observed as inset figures in Figure 1. The wavelength of maximum absorbance for the ligand in ethanol was observed at 327 nm. The wavelengths of maximum absorbance for complexes were observed at (374, 404, 382, and 375) nm for Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}, respectively. The number of absorptive species may also be determined by applying PCA on the data matrix shown in Figure 1.

Table 1 shows the PCA results on the experimental data. Table 1 presents the eigenvalues, ratios of consecutive eigenvalues, and RSD of the absorbance data matrix. The ratio of two consecutive eigenvalues is large at the second eigenvalue, so there are two principle components (absorptive species) in the absorbance data matrix for all complexes. One of the species is the ligand, and the other is the complex. Therefore, even for ML_2 complexes, the existence of two species (L and ML_2) was observed, and the ML species was not detected. Figure 2 shows the plots of singular values versus the number of components for complexes of Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} with PBHP in ethanol. The value of the stability constant for each complex was optimized by applying RAFA on the data matrix shown in Figure 1. The relationship between RSD and K_f for experimental data after processing RAFA on the absorption matrix is shown in Figure 3. The optimum stability constants of complexes are obtained where the RSD has the lowest value and the rank of the data matrix has been reduced by one. For example, a minimum RSD for the Co^{2+} complex at an optimized stability constant is 0.1049 as seen in Figure 3a.

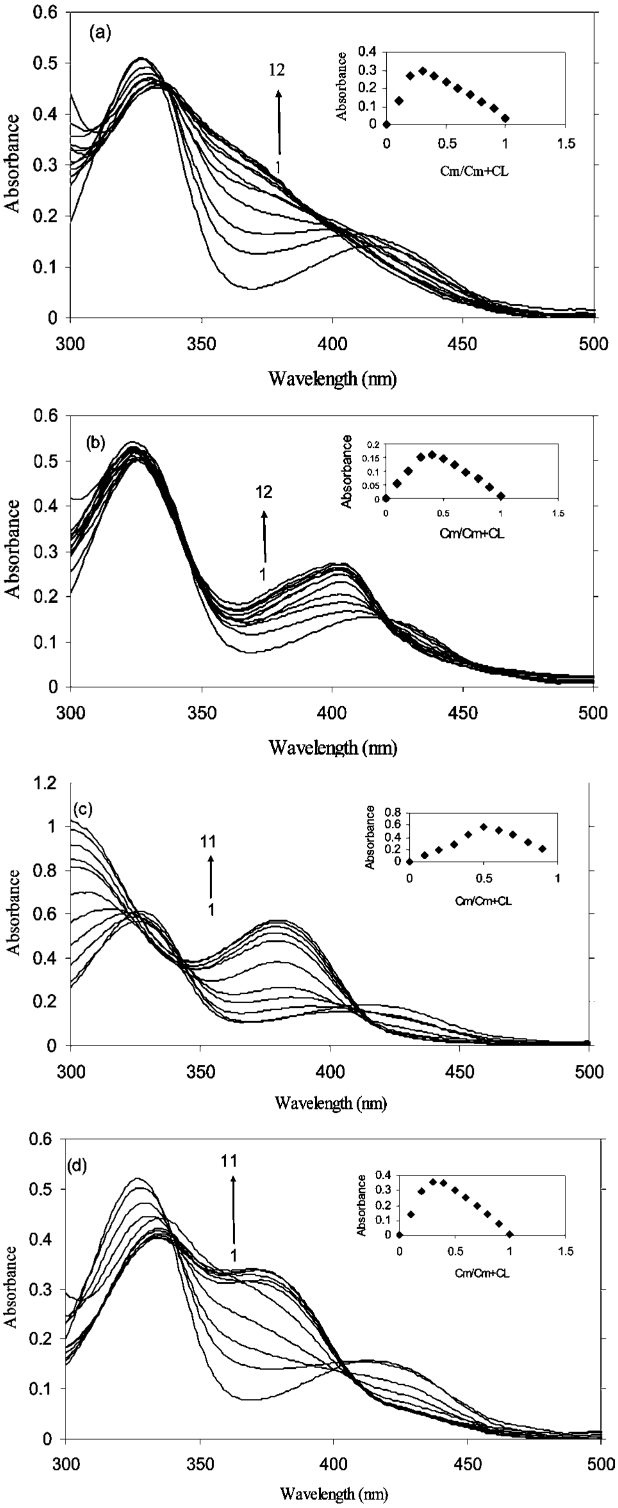


Figure 1. Experimental absorption spectra for (a) Co^{2+}, (b) Ni^{2+}, (c) Cu^{2+}, and (d) Zn^{2+} complexes with PBHP in ethanol. The analytical concentration of PBHP is $8.0 \cdot 10^{-5}$ (mol·L^{-1}) with different concentrations of metal in the range of 0.0 to 2.5 molar ratio of metal to ligand. The concentrations of metal are: (1) 0.0, (2) $8.0 \cdot 10^{-6}$, (3) $1.6 \cdot 10^{-5}$, (4) $2.4 \cdot 10^{-5}$, (5) $4.0 \cdot 10^{-5}$, (6) $5.6 \cdot 10^{-5}$, (7) 8.010^{-5}, (8) $9.6 \cdot 10^{-5}$, (9) $1.2 \cdot 10^{-4}$, (10) $1.44 \cdot 10^{-4}$, (11) $1.6 \cdot 10^{-4}$, and (12) $2.0 \cdot 10^{-4}$ (mol·L^{-1}).

Figure 4 shows the experimental absorption spectra for the complexes between PBHP and Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} in DMF, when the ligand concentration is constant and the metal

Table 1. Results of PCA on Experimental Data of Schiff Base Complex in Ethanol

	g_i				$g_i/(g_i + 1)$				RSD			
i	Ni	Co	Cu	Zn	Ni	Co	Cu	Zn	Ni	Co	Cu	Zn
1	140.82	140.26	255.14	110.17	186.66	58.458	27.643	28.796	0.38689	0.65639	1.2495	0.81426
2	0.75442	2.3993	9.2296	3.8259	8.5210	24.249	89.002	32.439	0.10944	0.12444	0.10721	0.11264
3	0.08853	0.09894	0.10370	0.11794	1.8699	2.0118	5.7563	4.4258	0.05537	0.06948	0.04360	0.04366
4	0.04734	0.04918	0.01801	0.02665	6.5442	1.4516	1.2221	4.4092	0.01808	0.03964	0.02599	0.01787
5	0.00723	0.03388	0.01474	0.00604	16.181	9.3330	12.681	3.8933	0.00450	0.01130	0.00700	0.00736
6	0.00045	0.00363	0.00116	0.00155	2.7510	17.859	3.7310	21.091	0.00215	0.00241	0.00298	0.00145
7	0.00016	0.00020	0.00031	0.00007								

concentration is varied. The molar ratio data and Job's plot for the investigated complexes showed a 1:2 metal-to-ligand stoichiometry for the Co^{2+}, Ni^{2+}, and Zn^{2+} complexes and a 1:1 metal-to-ligand stoichiometry for the Cu^{2+} complex. Job's plots for the Co^{2+}, Ni^{2+}, and Zn^{2+} complexes and molar ratio for Cu^{2+} complex are observed as inset figures in Figure 4. The wavelength of maximum absorbance for the ligand in DMF was observed at 326 nm. The wavelengths of maximum absorbance for complexes were observed at (373, 382, 382, and 372) nm for Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}, respectively. PCA results show that there are two principal components for all complexes in DMF (Schiff base and the complex). RAFA was applied on the data matrix shown in Figure 4, and stability constants of complexes were obtained at a minimum RSD.

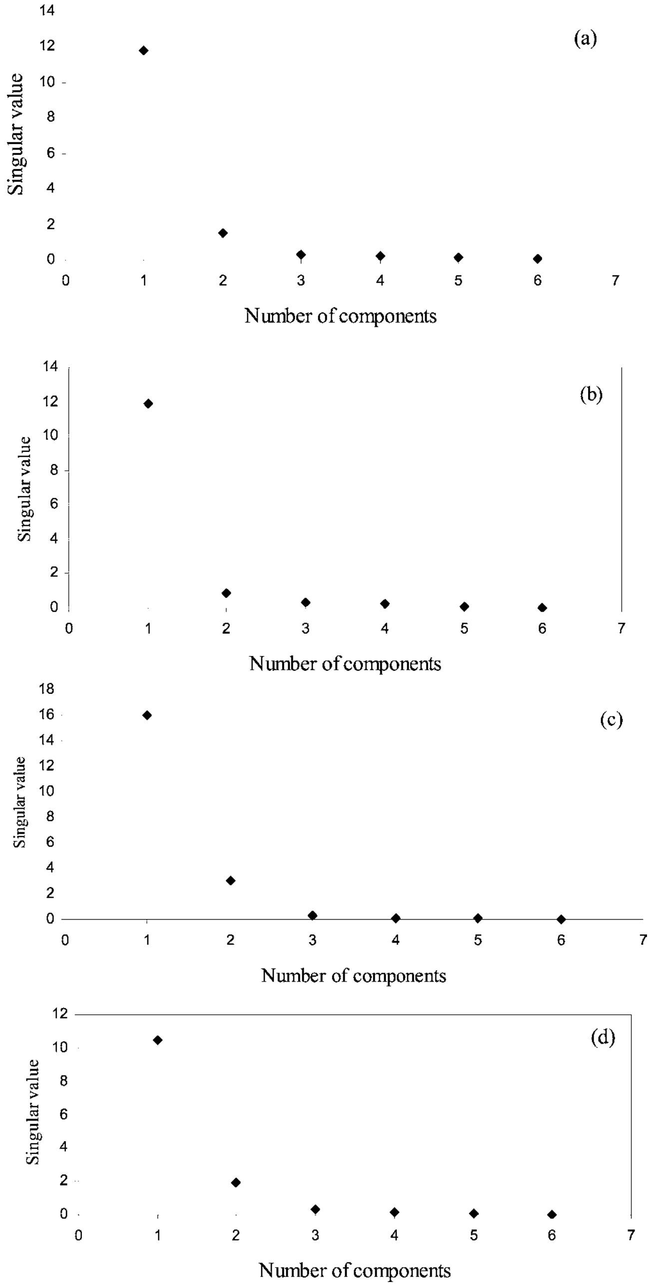


Figure 2. Plots of singular values versus the number of components for complexes of (a) Co^{2+}, (b) Ni^{2+}, (c) Cu^{2+}, and (d) Zn^{2+} with PBHP in ethanol.

Figure 5 shows the experimental absorption spectra for the complexes between PBHP and Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} in AN, when the ligand concentration is constant and the metal concentration is varied. The molar ratio data and Job's plot for the investigated complexes showed a 1:2 metal-to-ligand stoichiometry for the Co^{2+} and Ni^{2+} complexes and a 1:1 metal-to-ligand stoichiometry for the Cu^{2+} and Zn^{2+} complexes. Job's plots are observed as inset figures in Figure 5. The wavelength of maximum absorbance for the ligand in AN was observed at 325 nm. The wavelengths of maximum absorbance for complexes were observed at (360, 400, 382, and 373) nm for Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}, respectively. PCA results show that there are two principal components for all complexes in AN (Schiff base and the complex). RAFA was applied on the data matrix shown in Figure 5, and stability constants of complexes were obtained at a minimum RSD.

Table 2 shows the stability constants for Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} complexes with PBHP in ethanol, DMF, and AN. As seen in Table 2, Cu^{2+} forms 1:1 complexes with PBHP in all solvents; Co^{2+} and Ni^{2+} form 1:2 complexes in all solvents, and Zn^{2+} forms 1:2 complexes in ethanol and DMF and a 1:1 complex in AN. In ethanol the Co^{2+} complex has the largest value of the stability constant. In DMF, the Ni^{2+} complex has the largest value of the stability constant, and in AN the Co^{2+} complex has the largest stability constant. Complexes of Cu^{2+} have the lowest stability constants in ethanol and DMF because they form 1:1 complexes, and in AN, the lowest stability constant belongs to the Zn^{2+} complex, which is a 1:1 complex. Therefore, the type of solvent can have a great effect on the stoichiometry and stability constant of the complex.

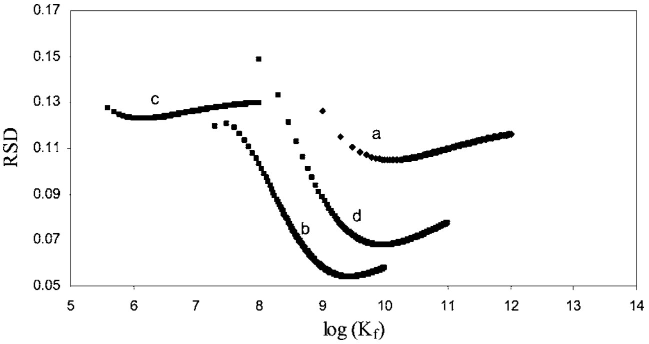


Figure 3. Relationship between RSD and stability constant, K_f, for (a) Co^{2+}, (b) Ni^{2+}, (c) Cu^{2+}, and (d) Zn^{2+} complexes with PBHP in ethanol.

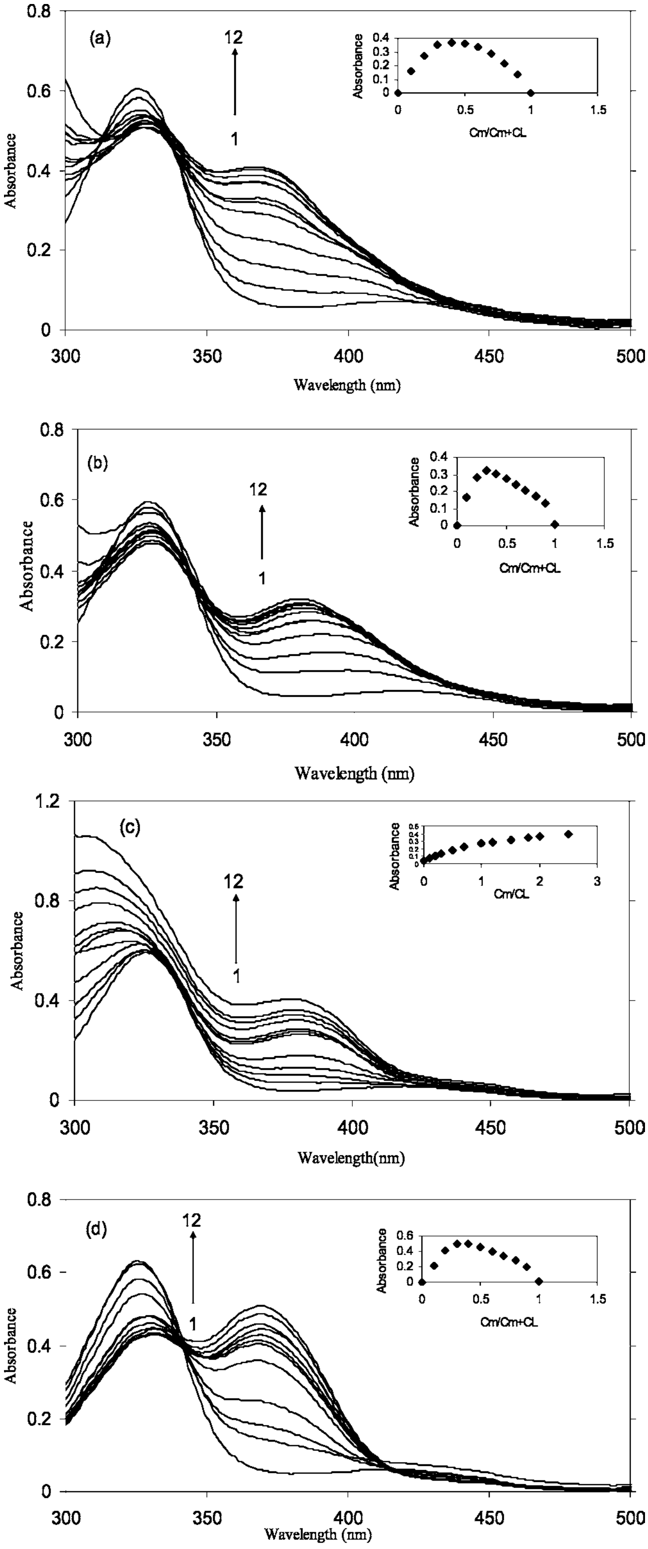


Figure 4. Experimental absorption spectra for (a) Co^{2+}, (b) Ni^{2+}, (c) Cu^{2+}, and (d) Zn^{2+} complexes with PBHP in DMF. The analytical concentration of PBHP is $8.0 \cdot 10^{-5}$ ($mol \cdot L^{-1}$) with different concentrations of metal in the range of 0.0 to 2.5 molar ratio of metal to ligand. The concentrations of metal are: (1) 0.0, (2) $8.0 \cdot 10^{-6}$, (3) $1.6 \cdot 10^{-5}$, (4) $2.4 \cdot 10^{-5}$, (5) $4.0 \cdot 10^{-5}$, (6) $5.6 \cdot 10^{-5}$, (7) $8.0 \cdot 10^{-5}$, (8) $9.6 \cdot 10^{-5}$, (9) $1.2 \cdot 10^{-4}$, (10) $1.44 \cdot 10^{-4}$, (11) $1.6 \cdot 10^{-4}$, and (12) $2.0 \cdot 10^{-4}$ ($mol \cdot L^{-1}$).

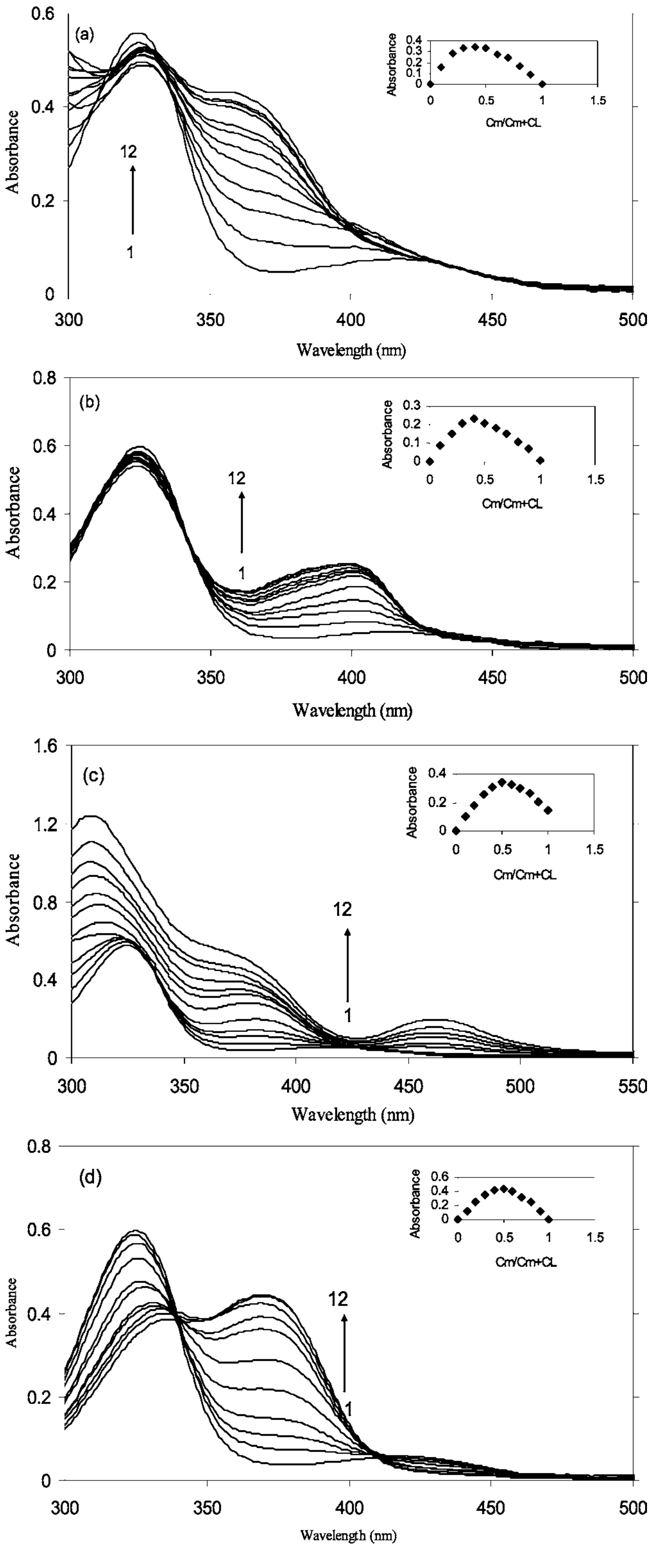


Figure 5. Experimental absorption spectra for (a) Co^{2+}, (b) Ni^{2+}, (c) Cu^{2+}, and (d) Zn^{2+} complexes with PBHP in AN. The analytical concentration of PBHP is $8.0 \cdot 10^{-5}$ ($mol \cdot L^{-1}$) with different concentrations of metal in the range of 0.0 to 2.5 molar ratio of metal to ligand. The concentrations of metal are: (1) 0.0, (2) $8.0 \cdot 10^{-6}$, (3) $1.6 \cdot 10^{-5}$, (4) $2.4 \cdot 10^{-5}$, (5) $4.0 \cdot 10^{-5}$, (6) $5.6 \cdot 10^{-5}$, (7) $8.0 \cdot 10^{-5}$, (8) $9.6 \cdot 10^{-5}$, (9) $1.2 \cdot 10^{-4}$, (10) $1.44 \cdot 10^{-4}$, (11) $1.6 \cdot 10^{-4}$, and (12) $2.0 \cdot 10^{-4}$ ($mol \cdot L^{-1}$).

Effect of Surfactants. The effect of anionic (SDS), cationic (CTAB), and neutral (Triton X-100) surfactants on the complexation reaction of Cu^{2+} with PBHP in DMF was studied. Table 3 shows the results of the complex formation constant of Cu^{2+} with PBHP in DMF for different concentrations of each surfactant.

The experimental data show that the stoichiometry of the formed complex does not change by adding the surfactant and

Table 2. Results of K_f for Metal−Schiff Base Complexes in Different Solvents[a]

	log K_f			
solvent	Co−L (ML_2)	Ni−L (ML_2)	Cu−L (ML)	Zn−L (ML, ML_2)
ethanol	10.100 ± 0.020	9.440 ± 0.020	6.150 ± 0.030	9.970 ± 0.017
DMF	9.290 ± 0.034	9.700 ± 0.023	5.390 ± 0.017	8.600 ± 0.084
AN	9.190 ± 0.019	8.660 ± 0.020	5.160 ± 0.014	5.047 ± 0.014

[a] L, Schiff base.

Table 3. Results of K_f for Cu−Schiff Base Complexes in DMF for Different Surfactants

SDS		CTAB		Triton X-100	
conc ($mol \cdot L^{-1}$)	log K_f	conc ($mol \cdot L^{-1}$)	log K_f	conc ($mol \cdot L^{-1}$)	log K_f
0	5.39 ± 0.01	0	5.39 ± 0.01	0	5.39 ± 0.01
$2.0 \cdot 10^{-3}$	4.84 ± 0.02	$5.0 \cdot 10^{-4}$	5.62 ± 0.02	$2.6 \cdot 10^{-3}$	5.68 ± 0.02
$4.0 \cdot 10^{-3}$	4.71 ± 0.01	$1.0 \cdot 10^{-3}$	5.74 ± 0.02	$5.2 \cdot 10^{-3}$	6.38 ± 0.03

also the spectra of ligand and complex do not change by adding the surfactant. As seen in Table 3, the addition of SDS caused a decrease in the stability constant. The decrease in stability of the complex of Cu^{2+} with the Schiff base in the presence of SDS is explained by a competition between ligand and head-groups of the surfactant.[31] Also, by increasing the concentration of SDS, the stability constant of the complex decreases more. The applied concentrations of SDS are below the cmc of SDS. Therefore, the observed effect relates to the surfactant molecule, not to micelles. CTAB and Triton X-100 increase the stability constant of the complex, and by increasing the concentration of CTAB and Triton X-100, the stability constant of the complex increases more. Also, the observed effect here relates to the surfactant molecule, not to micelles, because the concentrations of surfactants are below their cmc. There are some explanations for this effect of CTAB and Triton X-100 on the stability constant of complexes in the literature. One explanation is that an increase in the number of coordinated ligands happens in the presence of surfactants, which is explained by loosening of the hydration shell of a metal ion due to hydrophobic interactions.[32] In the case of Triton X-100, the formation of hydrogen bonds with ester oxygen atoms of the polyester chain is substantial, and the rather high strength of the complexes can also be the result of the interplanar interaction (stacking[33]) of benzene rings of coordinated ligands.[34]

Conclusions

RAFA is a powerful chemometric method to obtain the stability constants of complexes, especially when there is severe spectral overlapping. Also this method makes it possible to obtain pure absorption spectra and concentration profiles of species in several ligand−metal complex formation systems. 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 1:2 metal−ligand complex formations in different solvents, and the results show that the type of solvent has a great effect on stoichiometry and stability constant of the formed complexes. Also, the effect of surfactants on the stability constant of the complex of Cu^{2+} with the Schiff base in DMF was investigated, and it showed that SDS decreases the stability constant, CTAB and Triton X-100 increase the stability constant of the complex, and by increasing the surfactant concentration its effect will be higher for all three kinds of surfactants.

Note Added after ASAP Publication: This paper was published on the Web on August 3, 2010. Scheme 1 was revised. The corrected version was reposted on August 12, 2010.

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