

INVESTIGATION OF FORMATION CONSTANT OF COMPLEX OF A NEW SYNTHESIZED TRIPODAL LIGAND WITH Cu^{2+} USING RANK ANNIHILATION FACTOR ANALYSIS IN SURFACTANT MEDIA

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ABSTRACT. The complex formation between a newly synthesized tripodal ligand and the cation Cu^{2+} in water and surfactant media was studied spectrophotometrically using rank annihilation factor analysis (RAFA). According to molar ratio data the stoichiometry of complexation between the ligand and the cation Cu^{2+} was 1:1. Formation constant of this complex was derived using RAFA on spectrophotometric data. The performance of the method has been evaluated by using synthetic data. Also concentration and spectral profiles of ligand and complex can be obtained by using the stability constant and appropriate equations. The effect of surfactants such as sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB) and Triton X-100 on complex formation constant of Cu^{2+} with the ligand was investigated.

KEY WORDS: RAFA, Tripodal ligand, Complex formation constant, Surfactant

INTRODUCTION

Stability constants can be key parameters for the investigation of equilibria in solution. They are very important in many fields such as industrial chemistry [1], environmental studies [2], medicinal [3] and analytical chemistry [4]. Therefore complexation reactions of metal ions with different ligands have been widely studied [5-7]. Several methods for the determination of stability constants, such as potentiometric titration [8], conductometry [9], and spectrophotometric determination [10], 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. Chemometric methods can also easily resolve the overlapped spectra [11, 12], 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 [13]. It was modified by Lorber to yield a direct solution of a standard Eigen-value problem [14] 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 [15, 16], spectrophotometric determination of acid dissociation constants and the formation constants of metal–ligand complexation [17-19]. In this work we used RAFA for the determination of the stability constants of Cu^{2+} with the recently synthesized tripodal ligand.

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Theory

For the first time Abdollahi used RAFA for determination of complex formation constants [20]. The basis of the application of RAFA in the determination of the formation constants for 1:1 complexes was described in our previous work [21]. For a 1:1 metal ligand molar ratio complex the equations are as follows



$$K_f = \frac{[ML]}{[M][L]} \quad (2)$$

$$C_L = [L] + [ML] \quad (3)$$

$$C_M = [M] + [ML] \quad (4)$$

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. By substitution of [M] and [ML] from Eqs. (3) and (4) into Eq. (2) and rearranging yields

$$K_f [L]^2 + (K_f C_M - K_f C_L)[L] + [L] - C_L = 0 \quad (5)$$

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. It is important to mention that if the metal ion does not absorb in the wavelength range of study, the rank of the absorbance matrix will be 2. 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 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.

Based on principal component analysis (PCA), the RSD (relative standard deviation) method is widely used to determine the number of principal components [22, 23]. The RSD is a measure of the lack of fit of a principal component model to a data set. The RSD is defined as:

$$R.S.D.(n) = \left(\frac{\sum_{i=n+1}^c g_i}{n(c-1)} \right)^{1/2} \quad (6)$$

where g_i is the Eigen value, 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 placed in equation 5 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, then according to RSD equation (equation 6) the sum of Eigen values of the residual matrix is

obtained from Eigen value 2 to c (number of samples). If the rank of the residual matrix is reduced by one, the sum of Eigen values from Eigen value 2 to c will equal to noise level and 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

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 ligand was synthesized in the laboratory. Sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), Triton X-100 and chloride salt of Cu²⁺ were purchased from Merck (Darmstadt, Germany). 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 synthesis of tripodal ligand

The asymmetrical tripodal ligand (Figure 1) was prepared as its hydrochloride salts as we had synthesized in our previous work [24].

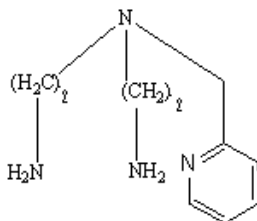


Figure 1. Structure of the tripodal tetradentate ligand.

Procedure

Stock solutions of ligand and metal ion salt were prepared in triple distilled water. The analytical ligand concentration was kept constant and different concentrations of metal ions were added to the ligand solution. The analytical concentration of ligand was 1.04×10^{-4} mol·L⁻¹ with different concentrations of metal in the range of 0.0 to 2.0 molar ratio of metal to ligand. The concentration of metal was: (1) 0.0, (2) 4.99×10^{-6} , (3) 9.98×10^{-6} , (4) 1.98×10^{-5} , (5) 2.5×10^{-5} , (6) 3.95×10^{-5} , (7) 5.93×10^{-5} , (8) 9.98×10^{-5} , (9) 1.2×10^{-4} , (10) 1.6×10^{-4} and (11) 2.0×10^{-4} (mol·L⁻¹). After preparation of the samples, the time of 1 hour was given to the samples until they reach to the stable mood. Then after 1 hour the spectrum of the sample solutions were obtained between 200 to 600 nm in the 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.

RESULTS AND DISCUSSION

Synthesis of complex

This is a tripodal tetradentate ligand with N4 donor atoms. Previously we have reported the synthesis and characterization of a number of macrocyclic [25] and macroacyclic [26, 27] metal complexes of above ligand. The X-ray single crystal structure of our synthesized complexes with different metal ions showed different structures. Herein we studied the formation constant of Cu^{2+} of ligand in solution phase. It should be noted that according to literature the best structure for the Cu^{2+} in the complex is described as distorted tetrahedral or trigonal bipyramidal [28].

Simulated data

Figure 2 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.

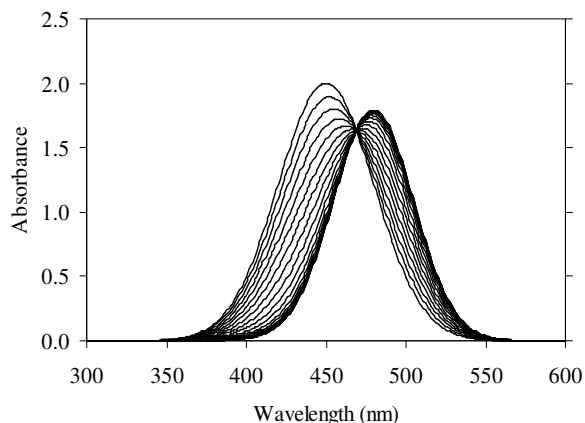


Figure 2. Simulated absorption spectra of a 1:1 metal-ligand complex formation system at a fixed concentration of ligand and various concentrations of metal ions. $\log K_f = 4.74$, $\lambda_{\max}(L) = 450 \text{ nm}$, $\lambda_{\max}(ML) = 480 \text{ nm}$.

Table 1 presents the Eigen values, ratios of consecutive Eigen values 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 3. A minimum is observed in the RSD curve shown in Figure 3 which indicates the optimum value of $\log K_f$. The applied noise was $\pm 0.1\%$ absorbance units.

Table 1. The results of PCA on simulated data.

i	g_i	g_i/g_{i+1}	RSD
1	2530	9.94	7.13
2	255	530416	0.013
3	0.00048	1.11	0.009
4	0.00043	1.07	0.006
5	0.0004	1.08	0.003
6	0.00037		

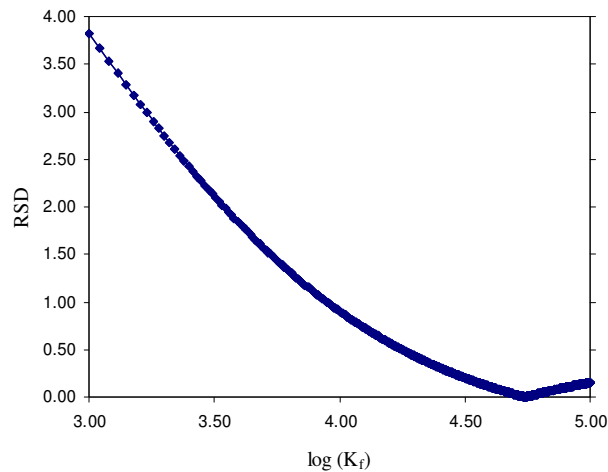


Figure 3. The relationship between RSD and stability constant, K_f , 1:1 complexation system obtained $\log(K_f) = 4.74$.

As seen in Table 1, the ratio of two consecutive Eigen values is too large at the second Eigen value, 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.

Real data

Figure 4 shows the experimental absorption spectra for the complex between the investigated ligand and Cu²⁺ when the ligand concentration is constant and the metal concentration is varied. PCA results showed that there are two principal components in the absorbance data matrix. Table 2 shows PCA results on experimental data. The relationship between RSD and K_f for copper experimental data after processing RAFA on the absorption matrix is shown in Figure 5. The optimum stability constant of complex is obtained where the RSD has the lowest value and the rank of the data matrix has been reduced by one. For example minimum RSD for Cu²⁺ complex at optimized stability constant is 0.3462 while the estimated complex formation constant after processing RAFA on the absorbance data matrix of Cu²⁺ was obtained as $4.15 \times 10^4 \text{ L mol}^{-1}$ (Figure 5).

Table 2. The results of PCA on experimental data.

i	g_i	g_i/g_{i+1}	RSD
1	200	11	1.91
2	18.2	280	0.085
3	0.065	8.12	0.023
4	0.008	38.54	0.003
5	0.00014	57.1	0.001
6	0.00006	0.42	

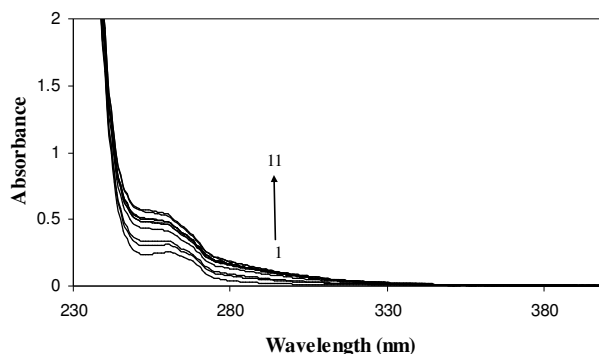


Figure 4. Experimental absorption spectra for the Cu^{2+} complex with the ligand. The analytical concentration of ligand is 1.04×10^{-4} ($\text{mol}\cdot\text{L}^{-1}$) with different concentrations of metal in the range of 0.0 to 2.0 molar ratio of metal to ligand. The concentration of metal is: (1) 0.0, (2) 4.99×10^{-6} , (3) 9.98×10^{-6} , (4) 1.98×10^{-5} , (5) 2.5×10^{-5} , (6) 3.95×10^{-5} , (7) 5.93×10^{-5} , (8) 9.98×10^{-5} , (9) 1.2×10^{-4} , (10) 1.6×10^{-4} and (11) 2.0×10^{-4} ($\text{mol}\cdot\text{L}^{-1}$).

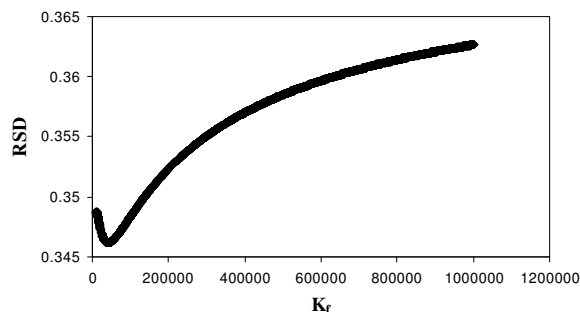


Figure 5. The relationship between RSD and stability constant, K_f for the Cu^{2+} complex.

Concentration and spectral profiles of the ligand and its complex with Cu^{2+} were obtained after processing RAFA on the absorbance data matrix of Cu^{2+} . Concentration profile of the ligand was obtained by giving the optimum K_f to equation 5 and then concentration profile of complex was obtained using equation 3. The spectral profiles of the ligand and its complex were obtained through the projection of the absorbance data matrix on to their concentration profiles matrix. These profiles can be seen in Figure 6

The effect of surfactants

The effect of anionic (SDS), cationic (CTAB) and neutral (Triton X-100) surfactants on the complexation reaction of Cu^{2+} with the ligand was studied. The stock solution of surfactants was prepared in distilled water, and then appropriate volume of stock solutions was added to the sample solutions in two ranges above and below of their critical micelle concentrations (cmc).

Table 3 shows the results of complex formation constant of Cu^{2+} with the ligand for different concentrations of each surfactant. As seen in Table 3 addition of SDS caused a decrease in the stability constant. The decrease in stability of complex of Cu^{2+} with the ligand in the presence of SDS is explained by a competition between ligand and head groups of the

surfactant [29]. Also by increasing the concentration of SDS, the stability constant of the complex decreases more. 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. There are some explanations for this effect of CTAB and triton X-100 on the stability constant of complexes in the literature [30]. 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 hydrate shell of a metal ion due to hydrophobic interactions [31]. 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 [25]) of benzene rings of coordinated ligands [32].

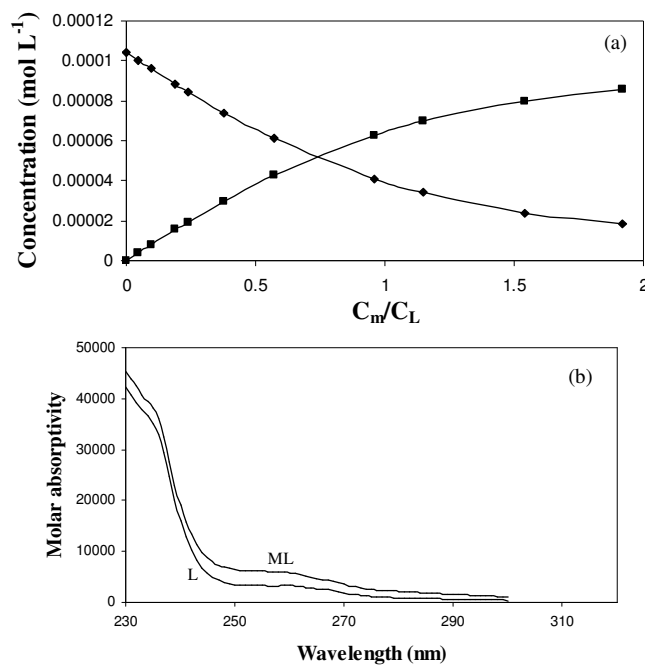


Figure 6. (a) Concentration profile of ligand and its complex with Cu²⁺ and (b) their spectral profile.

Table 3. The results of K_f for Cu-ligand complex for different surfactants.

SDS		CTAB		Triton X-100	
Conc. (mol L ⁻¹)	log $K_f \pm SD^a$	Conc. (mol L ⁻¹)	log $K_f \pm SD$	Conc. (mol L ⁻¹)	log $K_f \pm SD$
0	4.62±0.01	0	4.62±0.01	0	4.62±0.01
2.0×10 ⁻³	4.07±0.02	5.0×10 ⁻⁴	4.80±0.02	2.6×10 ⁻³	4.90 ±0.02
4.0×10 ⁻³	3.94±0.01	1.0×10 ⁻³	4.92±0.02	5.2×10 ⁻³	5.60 ±0.03

(a) Standard deviation for three replicate experiments.

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