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Spectrophotometric determination of the formation constants of some transition metal cations with a new synthetic Schiff base in dichloromethane and chloroform using rank annihilation factor analysis

Abbas Afkhami^{a,*}, Tayyebeh Madrakian^a, Hassan Keypour^a, Saeid Soltanbeygi^a, Farzad Khajavi^a, Majid Rezaeivala^b

^a Faculty of Chemistry, Bu-Ali Sina University, Hamedan 65174, Iran

^b Department of Chemical Engineering, Hamedan University of Technology, Hamedan 65155, Iran

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ABSTRACT

The complex formation between a new synthesized Schiff base and the cations Ni^{2+} , Co^{2+} , Cu^{2+} , Zn^{2+} in dichloromethane (DCM) and chloroform solutions was investigated spectrophotometrically using rank annihilation factor analysis (RAFA). The results of mole ratio plots and continuous variation data show the stoichiometry of complexation were found to be 1:1, and 2:1 metal ion to ligand. The stoichiometry was obtained as 1:1 metal ion to ligand ratio for Co^{2+} , Ni^{2+} and Zn^{2+} in chloroform and 2:1 for Cu^{2+} . In DCM the stoichiometry was obtained as 1:1 for Co^{2+} and 2:1 for Ni^{2+} and Zn^{2+} and a consecutive 2:1 metal ion to ligand ratio was obtained for Cu^{2+} . Formation constants of these complexes were estimated by application of RAFA on spectrophotometric data. In this process the contribution of ligand was removed from the absorbance data matrix when the complex stability constant acts as an optimizing object and simply combined with the pure spectrum of the ligand, the rank of the original data matrix.

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1. Introduction

Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications [1]. 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 [2]. It is known that the existence of metal ions bonded to biologically active compounds may enhance their activities [3,4].

Stability constants can be key parameters for the investigation of equilibria in solution. They are very important in many fields such as industrial chemistry [5], environmental studies [6], medicinal [7] and analytical chemistry [8]. Therefore complexation reactions of metal ions with different ligands have been widely studied [9–11]. Several methods such as potentiometric titration [12], conductometry [13], and spectrophotometry [14], have been reported for the determination of stability constants. 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 in the obtained results. This problem can be easily overcome using chemometric methods [15,16], 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 [17]. It was modified by Lorber to yield a direct solution of a standard eigen-value problem [18] 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 [19,20], spectrophotometric determination of acid dissociation constants and the formation constants of metal–ligand complexation [21–25]. 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.

2. Theory

The basis of the application of RAFA in the determination of the formation constants for 1:1 and 2:1 (metal to ligand) complexes was described in our previous works [24,25].



^{*} Corresponding author. Tel./fax: +98 811 8272404. *E-mail address:* afkhami@basu.ac.ir (A. Afkhami).

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For a consecutive 2:1 metal to ligand complexation reaction, the equations are as follows

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

$$ML + M \rightarrow M_2L$$
 (2)

$$K_{f1} = \frac{[\mathsf{ML}]}{[\mathsf{M}][\mathsf{L}]} \tag{3}$$

$$K_{f2} = \frac{[M_2 L]}{[ML][M]} \tag{4}$$

$$C_{L} = [L] + [ML] + [M_{2}L]$$

$$\tag{5}$$

$$C_{\rm M} = [{\rm M}] + [{\rm M}{\rm L}] + 2[{\rm M}_2{\rm L}] \tag{6}$$

where [L], [M], [ML] and [M₂L] are the equilibrium concentrations of ligand, metal ion and the complexes, respectively. K_{f1} and K_{f2} are the stepwise stability constants of the complexes, 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 combination of Eqs. (3)–(6) as a function of the free ligand concentration [L] yields

$$K_{f1}^{2} - 4K_{f1}K_{f2}[L]^{3} + (K_{f1}^{2}C_{M} - K_{f1}^{2}C_{L} - 4K_{f1}K_{f2}(C_{M} - 2C_{L}))[L]^{2} - (K_{f1}C_{M} + K_{f1}K_{f2}(C_{M} - 2C_{L})^{2} + 1)[L] + C_{L} = 0$$
(7)

If the values of C_M , C_L and K_{f1} and K_{f2} are known, it is possible to obtain the free ligand concentration [L] from the roots of the associated polynomial.

A two-way data matrix 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_{f1} and K_{f2} in Eq. (7) for a given amount of C_M and C_L , different vectors of ligand concentration will be obtained. The molar absorptivity of the ligand can be obtained from the spectrum of the pure ligand. Therefore the 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. RAFA uses the iterative procedure to find the best K_f so that 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 [26,27]. The RSD is a measure of the lack of fit of a principal component model to a data set. The RSD is defined as:

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

where g_i is the eigenvalue, n is the number of considered principal components and c is the number of samples. The RSD was used as a formula to obtain the optimum stability constant.

3. Experimental

3.1. 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. DCM, chloroform, diethyl ether, sodium sulfate, 3,5-di-tert-butylsalycilaldehyde, silica gel, chloride and nitrate salts of Ni²⁺, Cu²⁺, Co²⁺ and Zn²⁺ were purchased from Merck (Darmstadt, Germany) and *N*,*N'*-bis(3-aminopropyl)piperazine was supplied from Sigma–Aldrich Chemical Companies and used without further purification. All solutions were prepared freshly prior to the measurements. All calculations were performed in MATLAB 6.5 (Math Works, Cochituate Place, MA) and Microsoft Excel 2003.

3.2. General procedure for synthesis of Schiff base N,N'-bis (2-((3-propylimino)methyl)-4,6-di-tert-butylphenol)piperazine (PTBP)

3,5-Di-tert-butylsalicylaldehyde (1 mmol, 0.234 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 ¹H and ¹³C NMR spectra. Anal. Calc. for C₄₀H₆₄N₄O₂·0.5H₂O (MW: 632.5): C, 74.27; H, 10.77; N, 8.66. Found: C, 74.18; H, 11.10; N, 8.50%. Yield: 0.28 g (90%). m.p. (124.0-126.0) °C. IR (Nujol, cm-1): 1631 [v(C=N)], 1162(s) [v(C-O)]. MS (EI): $m/z = 632 [M]^+$. ¹H NMR (90 MHz, CDCl3, ppm) δH: 1.33 (s, 18H, H-3), 1.47 (s, 18H,7-H), 1.90 (b m, 4H,13-H), 2.51 (b m, 12H, 14-H and 15-H), 3.64 (t(3J = 8.0 Hz), 4H, 12-H), 7.10-7.39 (m, 4H, 1-H and 5-H), 8.37 (b s, 2H, -C=N), 13.89(s, 2H, --OH). ¹³C NMR (400 MHz, CDCl₃, ppm) δC: 28.1 (t, C-13), 29.4(q, C-3), 31.5(q, C-7), 34.1(s, C-4), 35.0(s, C-8), 53.3(t, C-15), 56.1(t, C-14), 57.6(t, C-12), 117.8 (s, C-10), 125.7, 126.8 (d, C-1, C-5), 136.7, 139.9 (s, C-2, C-6), 158.2 (s, C-9) (aromatic ring), 166.0(d, C-11, -C=N) [28]. Scheme 1 shows the structure of the synthesized Schiff base.

3.3. Experiment procedure

Stock solutions of PTBP and metal ion salts were prepared in DCM and chloroform. The analytical ligand concentration was kept constant and different concentrations of metal ions were added to the PTBP solution. Then after 30 min the spectrum of the solution was obtained between 270 and 500 nm in 1 nm intervals. The molar ratio data was 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.



Scheme 1. The structure of the synthesized Schiff base.

4. Results and discussion

4.1. Simulation for a 2:1 metal to ligand consecutive complexation reaction

Fig. 1 shows the simulated absorbance spectra of a 2:1 metalligand consecutive complex system at a fixed concentration of ligand $(8.0 \times 10^{-5} \text{ mol } L^{-1})$ and various concentrations of metal ion with molar ratios of 0-2.0 with a certain stability constant $(\log K_{f1} = 5.20 \text{ and } \log K_{f2} = 5.60)$. Concentration profiles of the ligand and complexes (ML and M₂L) were obtained through the appropriate equations. The pure spectra of the ligand and complexes were simulated by Gaussian function with the characteristics of: $\lambda_{max}(L) = 450$ nm, $\lambda_{max}(ML) = 500$ nm and $\lambda_{max}(M_2L) = 520$, spectral band width of 20 nm for ligand, 22 nm for ML complex and 25 nm for M₂L complex, and maximum molar absorptivity of 2500 L mol⁻¹ cm⁻¹ for ligand, 2200 L mol⁻¹ cm⁻¹ for ML complex and 2000 for M₂L complex. The simulated absorbance matrix was constructed by multiplying the concentration profiles matrix into the pure spectra matrix. Then the noise equal to ± 0.001 absorbance unit was added to the data matrix. PCA results show that there are three principal components in the absorbance data matrix. The synthetic data matrix was processed by the RAFA method and the relationship between the RSD of the residual matrix and the stability constants (K_{f1} and K_{f2}) is shown in Fig. 2.

4.2. Real data

The electronic absorption spectra of PTBP ligand between the cations of the first transition series (i.e. Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) in CHCl₃ solution are shown in Fig. 3. The PTBP ligand has an absorbance band with a λ_{max} at 329 nm, while each of cations does not show any absorption band in the investigated region. With the addition of M^{2+} ion to PTBP ligand solution, strong shift (50–55 nm) toward higher wavelengths in comparison to free PTBP ligand were observed where neither cation nor PTBP ligand have any absorption in this region. This is a clear indication for the formation of complexes. The absorption bands for Co^{2+} , Ni^{2+} and Zn^{2+} , mixtures appeared at 379, 387 and 383 nm, respectively, whereas the absorbance at 329 nm (due to PTBP ligand) decreased (Fig. 4).

The stiochiometry of complex was examined in CHCl₃ solution by the continuous variations method and found a maximum at X_{PTBP} value of 0.33 and 0.5 that emphasis on formation of a 2:1 Cu²⁺ – PTBP complex and 1:1 for Co²⁺, Ni²⁺ and Zn²⁺ ions in this solvent.

The PCA results show that 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 in CHCl₃. One of the species is the ligand and the



Fig. 1. Simulated absorbance spectra of a consecutive 2:1 metal–ligand complex formation system at a fixed concentration of ligand and various concentrations of metal ions. log K_{f1} = 5.20, log K_{f2} = 5.60, $\lambda_{max}(L) = 450$ nm , $\lambda_{max}(ML) = 500$ nm and $\lambda_{max}(M_2L) = 520$.



Fig. 2. The relationship between RSD and stability constants, K_{f1} and K_{f2} for a consecutive 2:1 metal–ligand complex formation system, obtained log (K_{f1}) = 5.20 and log (K_{f2}) = 5.60.



Fig. 3. Visible spectra of PTBP and its complexes with $Co^{2\ast},\,Ni^{2\ast},\,Cu^{2\ast}and\,Zn^{2\ast}$ in $CHCl_3$ solution.



Fig. 4. Experimental absorption spectra for $Ni^{2+}(1)$; PTBP (2) and complex with PTBP in chloroform with different concentrations of metal in the range of 0.0–2.0 M ratio of metal to ligand.

other is the complex. Therefore even for M_2L complexes, the existence of two species (L and M_2L) was observed and the ML species was not detected. The value of the stability constant for each complex was optimized by applying RAFA on the data matrix shown in Fig. 4.

Complexes in DCM showed a 1:1 metal to ligand stoichiometry for the Co²⁺ and a 2:1 metal to ligand stoichiometry for the Ni²⁺ and Zn²⁺. The wavelength of maximum absorbance for the ligand in DCM was observed at 329 nm. The wavelengths of maximum absorbance for complexes were observed at 379 nm, 384 nm and 382 nm for Co²⁺, Ni²⁺ and Zn²⁺ respectively. But, Cu²⁺ formed two complexes ML and M₂L in DCM solution which their wavelengths of maximum absorbance were 396 nm and 362 nm respectively. PCA results show that there are two principal components for Co²⁺, Ni²⁺ and Zn²⁺ complexes in DCM (Schiff base and the complex) and there are three principal components for Cu²⁺ complexes in DCM. (Schiff base, ML, and M₂L complexes). The plots of singular values versus number of components for the metal complexes in DCM are shown in Fig. 5. As seen in Fig. 5 there are three principal components for Cu²⁺ complex in DCM and there are two principal components for Co²⁺, Ni²⁺ and Zn²⁺ complexes in DCM.



Fig. 5. The plots of singular values versus number of components for complexes of: (a) Co^{2+} , (b) Cu^{2+} , (c) Ni^{2+} and (d) Zn^{2+} with PTBP in DCM.

Table 1

Formation constants estimated for Schiff base complexes with metal ions in two solvents.

Cation	Solvent			
	$CHCl_3 (D = 4.81^{a}, DN = 4.0^{b})$		DCM (D = 9.08^{a} , DN = 1.6^{b})	
	Metal/ligand	log K _f	Metal/ligand	log K _f
Co ²⁺	1:1	5.00 ± 0.02	1:1	6.30 ± 0.02
Ni ²⁺	1:1	5.60 ± 0.03	2:1	8.08 ± 0.02
Cu ²⁺	2:1	6.00 ± 0.01	1:1	5.47 ± 0.02
			2:1	4.83 ± 0.02
Zn ²⁺	1:1	5.65 ± 0.02	2:1	7.58 ± 0.03

^a D: dielectric constant (25 °C).

^b DN: Gutmann donor number.





Fig. 6. Concentration profiles (a) and spectral profiles (b) of the components of Cu²⁺ complex with PTBP in DCM.

RAFA was applied on the data matrices and stability constants of the complexes were obtained in minimum RSD Table 1 shows the stability constants for Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} complexes with PTBP in chloroform and DCM solutions.

Cu²⁺ forms a 2:1 metal to ligand complex in DCM and also the intermediate complex (ML) was seen in the absorbance data matrix. After applying RAFA on the data matrix and obtaining the stability constants (K_{f1} and K_{f2}), concentration profiles of the components (L, ML, M₂L) were obtained using the appropriate equations (Eqs. (3)–(6)), then by projection of absorbance data matrix on the concentration profiles, the spectral profiles were obtained using:

$$S = C^+ D \tag{9}$$

where C^* is the pseudo-inverse of the concentration matrix, *D* is the absorbance data matrix and *S* is the spectrum matrix. Fig. 6 shows the concentration and spectral profiles of the formed components of Cu²⁺ complex with PTBP in DCM.

From Table 1, it is obvious that the stability of the complexes in general was higher in DCM. It is well known that the Gutmann donor number and dielectric constant of solvents [29] is an important measure in complexation reactions. It should be noted that DCM, and CHCl₃ possess similar dipole moments (i.e. DCM: 1.55, CHCl₃; 1.01), but have quite different donor numbers. It is obvious that the stability of complex increases significantly by decreasing the donor number of the solvents. Therefore, as expected, the type of solvent can have a great effect on stoichiometry and stability constant of the complex.

It is worth noting that, in the case of complexation PTBP with the metal ions of the first transition series, the stability of the resulting complexes decrease in the order $Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+}$. This sequence follows the Irving–Williams order [30] which generally holds for equilibrium constants of different complexes of the metal ions of first transition series [31].

5. 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 2:1 metal-ligand complex formations in two solvents and the results show that the type of solvent has a great effect on stoichiometry and stability constant of the formed complexes.

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