Complexation Of P-Sulphonatocalix[4]Arene And Transition Metal In Optimized Temperature

K. Zare, N. Shadmani, Z. Yousefian

1Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran
2Department of Chemistry, Shahid Beheshti University, Evin, Tehran, Iran
3Young Researchers and Elite Club, Rasht Branch, Islamic Azad University, Rasht, Iran
Email: n.shadmani@gmail.com, Fax: +981315551007
4 Department of Chemistry, Shahre-Rey Branch, Islamic Azad University, Tehran, Iran

Abstract

At the present study, the complexation ability of the 25, 26, 27, 28-tetrahydroxy-5, 11, 17, 23-tetrasulphonic-calix[4]arene towards Tungsten (VI) was studied in aqueous solutions at temperature 298.15K using UV-Vis spectrophotometric method. A 1:1 complex was formed between calixarene and Tungsten (VI) ion. The $\Delta G^\circ$, $\Delta H^\circ$, and $\Delta S^\circ$ of reaction obtained and they were negative, means reaction is spontaneous, complex formation is exothermic and less disordering, respectively.

Keyword: Supramolecular chemistry; p-Sulphonatocalix[4]arene; Spectrophotometric method; Thermodynamic parameter

Introduction

Calixarenes are a group of macro cyclic compounds that contain phenolic units, which connected together by methylene bridges to form hydrophobic cavity [1-4]. They can be prepared by the base-induced reaction of certain p-substituted phenols with formaldehyde. The structure of calixarene characterized according to the methylene rotation [5-8]. In recent years, the water-soluble calix[n]arene derivatives have received considerable attention because of their selective metal ion binding properties in aqueous solutions, the formation of basket-like bilayer structures in the solid state, and the observation of OH hydrogen bonding [9-14]. There are many advantages for using calixarene as host molecules. Weak London forces, hydrogen bonding, $\pi-\pi$ interaction, and dipole-dipole moments play important roles in complex formation and drug release [15-18]. The studies about complex formation between p-sulphonatocalix[4]arene (SC4) with main elements, transition metals, anti-cancer and anti-HIV drugs as well as with additional organic supramolecular building components have been reported [19]. Calixarenes have been studied in the context of electrochemical selective sensor, liquid crystals, mimic enzyme, uranium extraction from sea [20-22], as stationary phases and as adsorbent in solid phase extraction [23]. P-sulphonatocalix[n]arene as a water-soluble calixarene may selectively include various guests according to its cavity size and hydrophobicity in a manner similar to cyclodextrins. Up to now, several Oxo and
Chloro tungsten (VI) complexes with calix[4]arene have been prepared. The new structures of some W(VI) calixarene complexes such as [W(tbcalix)(eg)] , [WO(tbcalix)] and [W(tbcalix)Cl₂] (tbcalix = tetravalent anion of p-tert-butyl calix[4]arene and eg = 1,2 ethanediolato dianion) were synthesized in 1998[24]. Complexes known to be suitable starting material to the calixarene supported organo tungsten complex [25-27]. In this work, the previously synthesized of the 25, 26, 27, 28-tetrahydroxy- 5, 11, 17, 23- tetrasulphonic calix[4]arene (Fig.1) was used to form stable complex with W(VI) ion in aqueous solutions and complexation parameters were obtained spectrophotometerically.

Material and Method

P-sulphonatocalix[4]arene was prepared from the Louis Pasteur University, France, (gratefully acknowledged), while Sodium tungstate dehydrate (99.9%), NaOH and HCl (titrazol 1N) were bought from Merck (Darmstadt, Germany) with pure analytical grades.

Absorption spectrum, in the wavelength range of between 280 nm and 310 nm, measured on a Scinco S-4100 (Korea) UV-Vis double beam scanning spectrophotometer using 1cm quartz cells. The temperature of system was controlled at 298.15K by circulating water from an isothermal bath. In all cases, the procedure repeated at least three times and the average of results used for calculations.

The titration of 2.5 ml solution of SC4 5×10⁻⁴ mol L⁻¹ was done with stepwise addition of the tungsten (VI) solution, between 1.5×10⁻² to 3.5 x 10⁻² mol L⁻¹, both of the same pH 7.1. A Jenway research pH-meter (model 827) used for the pH measurements. The hydrogen ion concentration measured with a Jenway combination electrode. The UV-Vis spectrum was of some combinations. These combinations have small changes in between 280 nm to 310 nm. The data measured with the computer using squad program. Fig. 2 shows the absorbance of mixture in the between wavelength of 280 nm and 310 nm. Complex formation studied with metal to ligand ratio \( \varphi = (0, 0.04, 0.08, 0.12, 0.16, 0.2, 0.24, 0.28, 0.32, 0.36, 0.4, \text{ and } 0.44) \) by stepwise titration of the certain concentration of SC4 with metal ion. The \( \varphi \) is representing the ratio of metal to ligand \( \left( \frac{M}{SC4} \right) \). The absorbance has decreased by increasing more amount of ion metal to SC4, Fig. 2. The variation of UV absorption spectrum of successive addition of W (VI) solution to SC4 solution at 280 nm and 310 nm.

Results and Discussion

Assuming that the absorbance of the SC4 would change upon complexation with the W (VI) metal ion, spectrophotometric measurements carried out. The formation of \( M_pSC4_q \) complex was characterized by changing its stoichiometry, \( p \) and \( q \), where \( M \) and SC4 represent metal ion and the ligand, respectively. The stability constant of complex, \( K_f \), defined according to Eq.1.

\[
\text{pM + qSC4} \rightarrow M_pSC4_q \quad K_f = \frac{[M_pSC4_q]}{[M]^p[SC4]^q} \quad (1)
\]

The stability constant was determined using the following method. Absorbance measured after addition of metallic ion to the SC4 solution. The absorption bands of the SC4 were decreased after addition of metal ion solution in the range.

of between 280 nm and 310 nm [28,29]. The stoichiometric stability constants calculated from the absorption data. The numbers of experimental points were more than 30 (maximum 40) for each titration. In the computer program, if we designate m absorption spectra that will measured at n wavelengths, the individual absorbance readings thus can arranged in an m × n matrix R; the m spectra form the R rows and the columns consist of the n response curves gathered at the different wavelengths. According to Beer’s law, for a system with N absorbing components, R can be decomposed into the product of a concentration matrix c (m ×N) and a matrix of the molar absorptivities S (N ×n). However, because of the inherent noise in the measured data, the decomposition does not represent R exactly. The matrix T of the residuals was given by the difference between CS and R, Eq.2.

\[ T = CS - R \quad (2) \]

In the fitting procedure, C and S matrices are determined in which represent the original matrix R best. The task of the fitting procedure is to optimize the matrix (T) of the residuals, Eq. 2. According to the least squares criterion in Eq.3, U is the sum of the squares of all elements of T. It is the task of the non-linear least squares fitting to find the set of parameters that result in minimum of U [30].

\[ U = \sum_{i=1}^{m} \sum_{j=1}^{n} T(i,j)^2 = \text{minimize} \quad (3) \]

It was prevented for other proposed species existed range of data. As expected poly nuclear, the computer program systematically rejected complexes. Taking into account a binuclear complex alone or together with mononuclear one does not improve the goodness of the fit and even leads to the rejection of the model. The model finally chosen, formed by MSC4, resulted in a satisfactory numerical and graphical fitting for all systems. The average stability constant (log \( K_f \)), \( \Delta H^\circ \), \( \Delta S^\circ \), and \( \Delta G^\circ \) of the 1:1 complex of SC4 with ion metal at specified wavelengths and 298.15K was listed in table 1. The standard enthalpy of reaction (\( \Delta H^\circ \)) tells us how much heat will flow in or out of the system. The standard Gibbs free energy (\( \Delta G^\circ \)) tells us whether a reaction will take place. The standard entropy of a reaction (\( \Delta S^\circ \)) tells us whether the products or reactants are more disordered. Standard Gibbs free energies at 298.15K calculated from Eq.4 and the results shown in table 1. The negative value of \( \Delta G^\circ \) shows a spontaneous forming complex. So, in lower temperatures complexes forms with, larger value of stability constant and lower value of standard Gibbs free energy. The results show that the best complexation temperature is 298.15K. According to van’t Hoff Eq.4 and Eq.5, \( \Delta H^\circ \), \( \Delta S^\circ \), \( \Delta G^\circ \) can calculate respectively. Where \( K_f \) is the solubility constant; \( \Delta H^\circ \), \( \Delta S^\circ \), \( \Delta G^\circ \) are the standard enthalpy, standard entropy, standard free Gibss energy respectively; T is absolute temperature; R is the universal gas constant.

\[ \ln K_f = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T} \right) + \frac{\Delta S^\circ}{R} \quad (4) \]

\[ \ln K_f = -\frac{\Delta G^\circ}{RT} \quad (5) \]

The curves of reaction between the SC4 and Tungsten (VI) (Fig. 3) show a sharp break point when the concentration ratio of metal ion to SC4 forms a stable complex. The \( \Delta G^\circ \), \( \Delta H^\circ \), and \( \Delta S^\circ \) of reaction obtained and they were
negative, means reaction is spontaneous, complex formation is exothermic and less disordering, respectively. Its great equilibrium constant ($K_f$) states high stability of complex $K_f = 10^{4.72}$ at 298.15K. According to the results more stable complex was formed at low temperatures.

Acknowledgements

Authors are grateful to University of Science and Research Branch, Islamic Azad University, Tehran, Iran. We are grateful to Shahid Beheshti University, Tehran, Iran. We are grateful to Young Researchers and Elite Club, Rasht Branch, Islamic Azad University, Rasht, Iran for supports.

Reference


phosphatidylcholine vesicles, Sens, 8: 6777-6790.


[21] Lehtonen, A., Sillanpää, R., 1994. Synthesis and crystal structures of bis(2,3-dimethyl-2,3-butenediolato)(1,2-ethanediolato)tungsten(VI) and tris(2,3-dimethyl-2,3-butanediolato)tungsten(VI), Polyhedron, 13: 2519-2524.


Table 1. The average Log K and thermodynamic functions (SI unite) at 298.15K.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Temperature</th>
<th>Log K</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC4-W(IV)</td>
<td>298.15</td>
<td>4.72±0.005</td>
<td>0.997</td>
</tr>
<tr>
<td>(\Delta H^\circ /\text{KJmol}^{-1})</td>
<td>-178.356</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\Delta G^\circ /\text{KJmol}^{-1})</td>
<td>-26.945</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\Delta S^\circ /\text{KJmol}^{-1}K^{-1})</td>
<td>-0.508</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. The Structure of 25,26,27,28 tetra hydroxy-5,11,17,23 tetrasulphonic calix[4]arene.
Complexation of P-Sulphonatocalix[4]Arene

Fig. 2. The variation of UV absorption spectrum of successive addition of W (VI) solution to SC4 solution at 280 to 310 nm.

Fig. 3. Spectrophotometric titration plots of the SC4 by metal ion at 298.15 K and 280 nm.