Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 6 (3) 191-194: Fall 2009
(J.Phys.Theor.Chem. IAU Iran)
ISSN: 1735-2126

Spectrophotometric Studies of Vanadium(III) Ion Complexes with p-Sulfonatocalix[4] arene in Aqueous Solution

Karim Zare, [1, 2]* Meysam Shirmohammadi,[1] Morteza Keshavarz[3] and Farrokh Gharib[2]

[1] Chemistry Department , Science and Research Branch, Islamic Azad University, Tehran, Iran
[2] Chemistry Department, Shahid Beheshti University, Tehran, Iran
[3] Chemistry Department, Shahreza Branch, Islamic Azad University , Shareza,Iran

ABSTRACT

Spectrophotometric technique is used to evaluate binding of the vanadium(III) ion to a water soluble calix[4] arene molecule in aqueous solution. On the basis of the calculated value formation constant at 25°C,we found that the complexation of this metal ion is very favored towards 25, 26, 27, 28-tetrahydroxy-5, 11, 17, 23-tetrasulphonalic acid-calix[4]arene
Gaussian 03 package.

Keywords: P-sulfonatocalix[4] arene; Vanadium(III); Spectrophotometry; Aqueous solution

INTRODUCTION

Calixarenes are synthetic macrocycles obtained by the condensation of p-substituted phenol and formaldehyde in alkaline medium. Lower and upper rim functionalisation of the parent calixarenes had led to a large variety of derivatives. Their bowl-like structure allows them to form complexes with a variety of species[1] Fine control of the size of calix[n]arenes, by changing the value of n and the introduction of various functional groups makes it possible to prepare a variety of molecules with various applications. Calixarenes are of interest to chromatography, slow release of drugs, transport across membranes, ion channels, and many other applications [2-5].

It has been shown recently, using rigidified calix[4]arenes, that its complexation properties depend not only on the nature of the donor groups but also on their stereo-chemical arrangement,can be characterized by the conformation of the calixarenes [6-7].

Depending upon the relative orientation of the para and phenolic sites, the tetramer can adopt four different conformations: cone, partial cone, conformer of calix[4]arenes shows usually the highest affinity for Na^+, whereas the partial cone and 1,3-alternate conformers show the best selectivity for K^+ and Cs^+[8] While several calixarene-metal cation complexes have been reported, most of them require that the hydroxyl groups of the calixarene be derivatized to esters or ethers[9] because of the poor solubility of the p-tertbutyl-calixarenes. The Cs^+-p-tertbutyl-calixarene complex is used for the recovery of cesium from nuclear waste solutions [10], and as a lanthanide complexing agent under basic conditions [11] Derivatives other than ethers and esters have been examined: calixcrowns show a high Na^+/Cs^+ selectivity, and are used as carriers through supported liquid membranes [10] The conformation of the calixarene in these complexes is normally a cone, except when derivatization forces other conformations, as in the case of 1,3-calix[4]bis-crown, which shows an alternate 1,3 conformation [10] There is evidence of some conformational freedom for the metal complexes in solution [12] Alkyl ketone residues have been introduced in the lower rim of calix[5]arene and calyx [6] arene [13] which show affinity for

---

* Corresponding Author: kmzare@gmail.com

complexation of alkali metal cations. Phosphoryl and amide ligands, both at the lower and upper rim, facilitate extraction of lanthanides and actinides [14-15].

In this work, stability constant of vanadium(III) cation and 25, 26, 27, 28-tetrahydroxy-5, 11, 17, 23-tetrasulphonalic acid-calix [4] arene were determined in aqueous solution at 25 °C using spectrophotometric technique. The structure of the studied calixarene is shown in Figure 1. The calixarene in this study was consistsed of four benzene rings which are arranged conically, so that hydroxyl and the sulphonato groups form a coordination sphere where metal cations can be bound.

EXPERIMENTAL

Chemicals. 25, 26, 27, 28-tetrahydroxy-5, 11, 17, 23-tetrasulphonalic acid-calix[4]arene where obtained as a gift (from Professor Zare) and used without further purification. Vanadium(III) chloride was purchased from Merck as analytical reagent grade material and was dried under vacuum at room temperature for at least 72 hours before use. All dilute solutions were prepared from double distilled water with a specific conductance equal to $1.2 \pm 0.1\ \mu Scm^{-1}$.

Measurements. The M 350- double beam UV-Vis spectrophotometer model of campec equipped by Pentium (2) computer. In all cases, the procedure was repeated at least three times and the resulting average values and corresponding error from the average are shown in the text and Tables.

Procedure. 2.5 cm^3 solution of the ligand, 1.0×10^{-3} mol dm^{-1}, was titrated with stepwise addition of the vanadium(III) solution, $(2.0\text{-}8.0)\times10^{-4}$ mol dm^{-3}, both in aqueous solutions.

RESULTS AND DISCUSSION

Assuming that the absorbance of the ligand would change upon complexation with the V(III) metal ion, we performed spectrophotometric measurements. The complex M_pL_q formation was characterized by changing its stoichiometry, p and q, where M and L represent each metal ion and the ligand, respectively. Considering that the formation constant of complexation, K_S, is defined equation 1.

$$pM + qL \;=\; M_pL_q \quad K_S = [M_pL_q] / [M]^p[L]^q \qquad (1)$$

The method of determination of formation constant has been described before [16] The absorbance, A, was measured for the solutions, as described in experimental section. For calculating of the formation constants, the spectrophotometric titration data were analysed at a wavelength in UV range that is given by

$$A = \varepsilon_M[\text{metal ion}] + \varepsilon_L[L] + \varepsilon_C[\text{complex}] \qquad (2)$$

where ε_M, ε_L, and ε_C are the molar absorptivities of the metal ion, ligand, and the formed complex, respectively. For the mass balance [metal ion] =

$$C_M - [\text{complex}] \qquad (3)$$

$$[L] = C_L - [\text{complex}] \qquad (4)$$

where C_M and C_L are the total concentration of the metal ion and the ligand, respectively. Substituting eqs 1 and 3-4 into eq 2 and rearranging and canceling like terms in a wavelength that the metal ion has actually no absorbance gives

$$A=C_L\varepsilon_L-C_M\varepsilon_L-C_L\varepsilon_M+C_M\varepsilon_M+C_L\varepsilon_C+C_M\varepsilon_C-\varepsilon_L/K_S-\varepsilon_M/K_S+\varepsilon_C/K_S\pm\varepsilon_L B\pm\varepsilon_M B\pm\varepsilon_C B)/2 \qquad (5)$$

where B is equal to $(1 + 2C_LK_S + 2C_MK_S + C_L^2K_S^2 - 2C_LC_MK_S^2 + C_M^2K_S^2) / K_S$. Using a suitable computer program [17] the data were fitted to eq 5 for estimating the formation constant of eq 1. We used the Gauss-Newton nonlinear least-squares method in the computer program to refine the absorbance by minimizing the error squares sum from eq 6,

$$S = \Sigma(a_i - b_i)^2 \qquad (i = 1, 2, 3, \ldots) \qquad (6)$$

where a_i is an experimental quantity and b_i is a calculated one. The computer program consisted of two different kinds of fitting, graphical and numerical. The final selection of the species was based on both graphical and numerical methods, considering in addition the various statistical criteria, i.e. sums of squared residuals, differences of C_M (experimental) and C_L (experimental) from those of calculated one. Figure 2 shows a typical example of a graphical fitting for the observed and calculated absorbances (from the computer program).

It was checked for other proposed species existed in significant concentration over a reasonable range of data. As expected polynuclear complexes were systematically rejected by the computer program. Taking into account a binuclear complex alone or together with the 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 ML, resulted in a satisfactory numerical and graphical fitting. The average value of the formation constant for the 1:1 complex species of the various wavelengths used is listed in Table 1.

The interesting curve resulting from the spectrophotometric titration of the ligand by vanadium(III) (Figure 3) shows a sharp break point when the concentration ratio of metal ion to the ligand reaches unity, indicating the formation of a stable complex for the metal ion.

Table 1. Average value of log K_S in different wavelengths for the calixarene and vanadium(III) ion at 25 °C

metal ion	lng K_S
vanadium(III)	5.59 ± 0.15

wavelength	logKs
280	6.13
275	5.68
270	5.45
265	5.31
260	5.44
255	5.55

The average amount of calculated formation constant was 5:59. V(III) shows that electric charge effect on metal is more the electrostatic force is stronger so the formed complex is stronger.

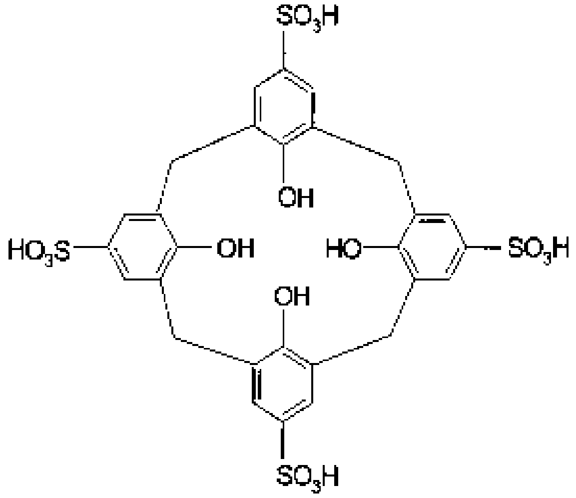

Fig. 1. The shematic structure.

25,26,27,28 tetrahydroxy- 5, 11, 17, 23 thtrasulphonulic acid- calix (4) arene.

The structure of the studied calix arene is show in figure 1. The calix arene in this study consists of four benzene rings which are arranged conically. So that hydroxyl and the sulphonato groups from a coordination sphere where metal cations can be bound.

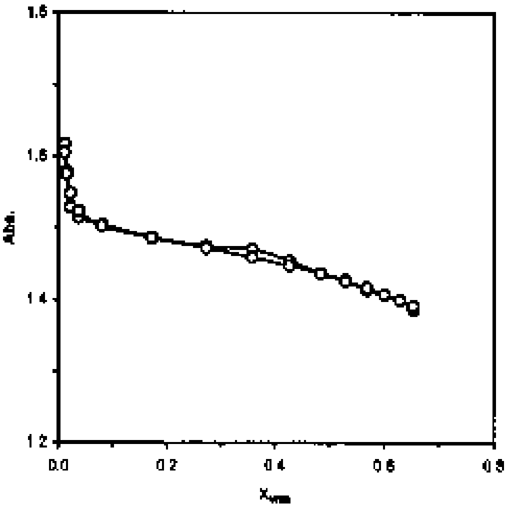

Fig. 2. A typical graphical fitting for V(III) + L system at 25 °C and 280 nm. (a) experimental absorbance, (b) calculated absorbance from the computer program.

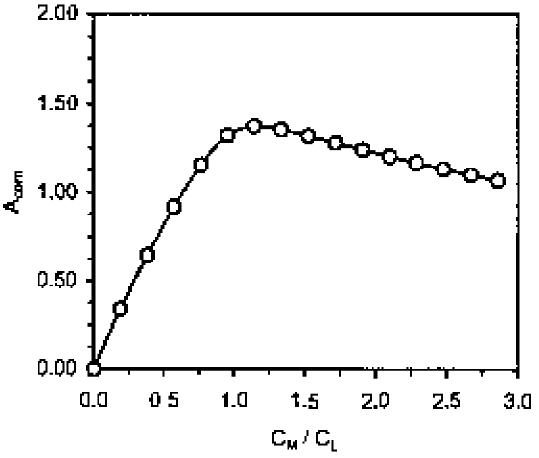

Fig. 3. Spectrophotometric titration plot of the ligand by the metal ion at 25 °C and 280 nm.

Average amounts of log k_s of ligand and metal at different wave lengths are listed in fig.3.
According ro figure3, the molar ratio of ligand ro meta lis 1:1.

Table 2. The rstio of metal ion to ligand concentrations versus of complex absorbances at 257 nm

C_m/C_L	$A_{Complex}$
0.0	0
0.2	0.34
0.4	0.64
0.6	0.92
0.8	1.15
1.0	1.32
1.1	1.38
1.4	1.36
1.5	1.32
1.7	1.28
1.9	1.24
2.1	1.20
2.3	1.17
2.5	1.13
2.7	1.10
2.9	1.07

We concluded that , the molar ratio of ligand to metal was 1:1. The average amount of calculated formation constant was 5.59. the more electric charge effects on metal V(III) is the electrostatic force is stronger so the formed complex is stronger.

We found also is no proton at pH=3.2 and negative charge is settled in lattice. There are four negative head and there are has three positive charges also vanadium ion so stronger electrostatic bond is formed. The stability constants of obtained complexes depend on two groups of upper rim and lower rim as well as size of rings. Amounts of equilibrium constants in L_1 ligand indicate that phenyl rings of calix with π electrons are agent of complexing.

CONCLUSION

REFERENCES

[1] Danil de Namor, A. F.; Casal, A. F.; Pugliese, A.; Goitia, M. T.; Montero, M. *J. Chem. Soc. Faraday Trans.* **1997**, 93, 3955.

[2] Benevelli, F.; Kolodziejski, W.; Wozniak, K.; Klinowski, J. *Chem. Phys. Let.* **1999**, 308, 65.

[3] Thuery, P.; Nierlich, M.; Asfari, Z.; Vicens, J. *Polyhedron* **2000**, 19, 1749.

[4] Jin, T.; Kinjo, M.; Koyama, T.; Kohayashi, Y.; Hirala, H. *Langmuir* **1996**, 12, 2684.

[5] Chiba, M.; Kim. H.; Kitamura, N. *J. Photochem. Photobiol.* 2002, 151, 67.

[6] Arnaud-Neu, F.; Asfari, Z.; Souley, B.; Vicens, J. *New J. Chem.* **1996**, 20, 453.

[7] Danil de Namor, A. F.; Gil, E.; Tanco, M. A.; Tanaka, D. A.; Salazar, L. E.; Schulz, R. A.; Wang, J. *J. Phys Chem.* **1995**, 99, 16776.

[8] Meier, U. C ; Detellier, C. *J Phys. Chem. A* **1998**, 102, 1888.

[9] Danil de Namor, A. F.; Gil, E.; Margot, A.; Tanco, A. L. *J Phys. Chem.* **1995**, 99, 16781.

[10] Arnaud-Neu, F.; Schwing-Weill, M. J. *Synthetic Metals* 1997, 90, 157.

[11] Arnaud-Neu, F.; Barrett, G.; Cremin, S.; Deasy, M. *J. Chem. Soc. Perkin Trans.* 1992, 1119.

[12] Buschmann, H.; Wenz, G.; Cleve, E.; Schollmeyer, E. *Acta Chim. Slov.* **2000**, 47, 55.

[13] Bell, S.; Browne, J.; McKee, V.; McKervey, M. A.; Malone, J. *J. Org. Chem.* **1998**, 63, 489.

[14] Asfari, Z.; Wenger, S.; Vicens, J. *Supramolec. Sci.* 1994, 1, 103.

[15] Arnaud-Neu, F.; Barrett, G.; Fanni, S.; Marrs, D. *J. Chem. Soc. Perkin Trans.* **1995**, 453.

[16] Gharih. F.; Zare, K.; Taghvaei, S.; Monajjemi, M.; Amiri, A. *Main Group Met. Chem.* In Press, 2084.

[17] Harris, D. C. *J. Chem. Edu.* **1998**, 75, 119.