

**Thermodynamic study of dioxovanadium (V) Complexes with
p-sulphonato-calix [6] arene in aqueous solution**

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ABSTRACT

The complexive ability of *p*-sulphonato-calix[6]arene towards dioxovanadium(V) has been evaluated in acidic aqueous solution (pH 1.7) using UV–Vis spectrophotometric technique. The result showed that the ligand is capable to complex with the oxo-cations by 1:1 cation to ligand ratios. Formation constant of the system has been determined at different temperatures (25 to 40°C). Considering the formation constant values, the binding selectivity of the ligand towards the oxo-cations at 25 °C is in the order VO₂⁺. The thermodynamic parameters have evaluated and are interpreted in terms of the importance of the various interactions responsible for the complexation. A roughly linear relationship between ΔH° and TΔS° has been observed for the studied systems and those were reported in the literature. Finally, the host and guest desolvation involved in the complexation processes are discussed. In conclusion, this study demonstrated the efficiency of the calixarene emulsion, which can be regarded as a promising treatment for dioxovanadium cutaneous contamination.

Keywords: P-sulphonato-calix[6]arene; Dioxovanadium(V); Aqueous solution; Formation constant

INTRODUCTION

Calix[n]arenes are one of the three major groups of organic macrocyclic host compounds in supramolecular chemistry [1]. They are composed of phenol units connected by ortho-methelene bridges and may complex to a variety of guests in solution as well in the solid state [2]. Controlling the size of the molecule (by changing the value of n) and introduction of various functional groups makes the calix[n]arenes useful for a variety of applications, such as catalysts, ligands as molecular hosts, slow releasers of drugs, transporters across membranes, ion channels, for purification, chromatography,

etc. [3–7]. Calixarenes are synthetic macrocycles obtained by the condensation of *p*-substituted phenol and formaldehyde in alkaline medium. Lower and upper rim fictionalization 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 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,

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transport across membranes, ion channels, and many other applications [8]. Several calix[n]arene-metal ion complexes have been reported, most of them require that the hydroxyl groups of the calixarene are derivatized to esters or ethers due to the poor solubility of the para-tert-butylcalix[n]arenes [9]. In general, the crystal structures of *p*-sulfonatocalix[4]arenes typically adopt a cone conformation, which is composed of a sandwich-like interleaved structure of organic layer and inorganic layer[10]. The X-ray crystal structures of *p*-sulfonatocalix[6]arenes, by contrast, adopt either an ‘up-up’ double partial cone conformation or an ‘up-down’ double partial cone conformation, so revealing conformational flexibility. The properties of *p*-sulfonatocalix[6]arenes seem to be controlled by the combination or stoichiometry of organic ligand compounds and lanthanide metal cations[11]. Hexacid calixarene, also known as uperuranophile, is a metal complex of derivatized calixarene used for the recovery of uranium [12] present work complexation ability of calix[6]arene toward dioxovanadium(V) are reported in aqueous solution at pH 1.7 and different temperatures.

EXPERIMENTAL

Chemicals

P-hexasulphonato-calix[6]arene was obtained from Acros Organics, Fig. 1, sodium monovanadate and were purchased from Merck (p.a.) and used without further purification. All dilute solutions were prepared from double distilled water with a specific conductance equal to $1.2 \pm 0.1 \mu\text{Scm}^{-1}$.

Measurements

A Jenway research pH-meter (model 827)

was used for the pH measurements. The hydrogen ion concentration was measured with a Jenway combination electrode. The pH-meter was calibrated with Metrohm pH 4.0 and 7.0 buffers leading to pH estimate error of ± 0.001 pH units. Spectrophotometric measurements were performed using a UV-Vis Cary 300 scanning spectrophotometer with a Pentium4 computer using 10 mm quartz cells. The system was thermostated at 25 °C by circulating water from an isothermal bath. For each experiment, a 2 mL solution of the ligand, $2.0 \times 10^{-4} \text{ mol dm}^{-3}$, was titrated with stepwise addition of 2 mL of metal cation solution $(3.0-4.0) \times 10^{-4} \text{ mol dm}^{-3}$, both of the same pH 1.7. The procedure has been repeated at pH 1.7 in different temperatures of 25 to 40 °C. The pH of solutions was controlled by adding appropriate volume of a diluted hydrochloric acid to the test solutions to acquire the desired pH. In the titration procedure after addition of a few drops of titrant, the absorbance was measured in the range 250–400 nm (in the interval of 1 nm) and the procedure extended up when the ratio of the metal ion to the ligand concentrations reaches to 2. The UV-Vis spectra of the mixtures undergo small changes but the measured absorbances were sufficient to allow the treatment of the data with the computer program.

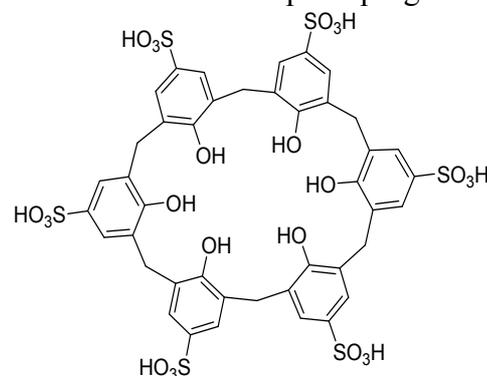
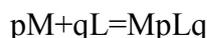


Fig. 1. The structure of *p*-hexasulphonato-calix[6]arene.

In all cases, the procedure was repeated at least three times, and the resulting average values and corresponding deviations from the average are shown in the text and Tables. To exclude carbon dioxide from the system, a stream of purified nitrogen was passed through a sodium hydroxide solution and then bubbled slowly through the reaction solution.

RESULT AND DISCUSSION

Assuming that the absorbance of the ligand would change upon complexation with a metal cation, we performed spectrophotometric measurements. The complex M_pL_q formed is characterized by its stoichiometry, p and q , where M and L represent a metal ion and the ligand, respectively. To determine the formation constant of complexation, K_S , Eq. (1) is defined,



$$K_S = \frac{[M_pL_q]}{[M]^p[L]^q} \quad (1)$$

Determination of the formation constant was employed using the method described before. Absorbance, A , was measured by successive addition of a metal ion solution to the ligand solution. The observed absorption bands of the ligand increase in the case of dioxovanadium(V) upon addition of the metal ion solution in all cases, Figs. 2. The changes of the absorbance in Figs. 2 are the result of dilution due to the titration procedure and complex formation and the extinction of the complex is different from the one of the ligand. Treatment of the spectrophotometric data obtained during the titrations was conducted with the computer program Squad.

The stoichiometric formation constants were computed from the data using the

computer program. The number of experimental points was more than 40 (maximum 50) for each titration.

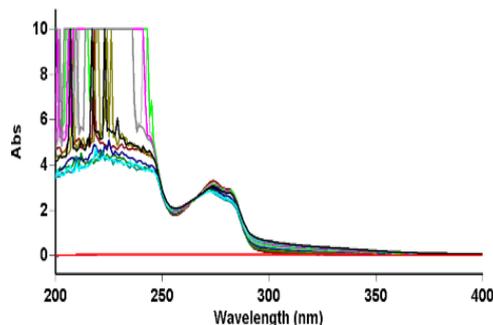


Fig. 2. Changes in UV-Vis absorption spectra of the ligand (lower curve) upon addition of VO_2^+ at 25 °C and pH 1.7.

In the computer program, if we designate m absorption spectra that will be measured at n wavelengths, the individual absorbance readings thus can be arranged in an $m \times n$ matrix \mathbf{R} ; the m spectra form the rows of \mathbf{R} 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, \mathbf{R} can be decomposed into the product of a concentration matrix \mathbf{C} ($m \times N$) and a matrix of the molar absorptivities \mathbf{S} ($N \times n$). However, because of the inherent noise in the measured data, the decomposition does not represent \mathbf{R} exactly. The matrix \mathbf{T} of the residuals is given by the difference between \mathbf{CS} and \mathbf{R}

$$\mathbf{T} = \mathbf{CS} - \mathbf{R} \quad (2)$$

In the fitting procedure, those matrices \mathbf{C} and \mathbf{S} are determined which best represent the original matrix \mathbf{R} . The task of the fitting procedure is to optimize the matrix \mathbf{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 \mathbf{T} . It is the task of the nonlinear least-squares fitting to find the

set of parameters that result in a minimum of U .

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

All proposed species existing in significant concentration were checked 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 quality of the fit and even leads to the rejection of the model.

and graphical fitting for the studied systems. The formation constant of the 1:1 complex species are listed in Table 1 at different temperatures. The interesting curves resulting from the spectrophotometric titration of the ligand with the cations are shown in Fig. 3. The curves show a sharp break point when the ratio of the concentration of metal ion to the ligand reaches unity, indicating the formation of stable complexes for VO_2^+ . In these cases the extrapolating of the slopes at high and low metal to ligand ratios correspond to 1:1 complex stoichiometry in the point of intersections.

The model finally chosen, formed by ML, resulted in a satisfactory numerical

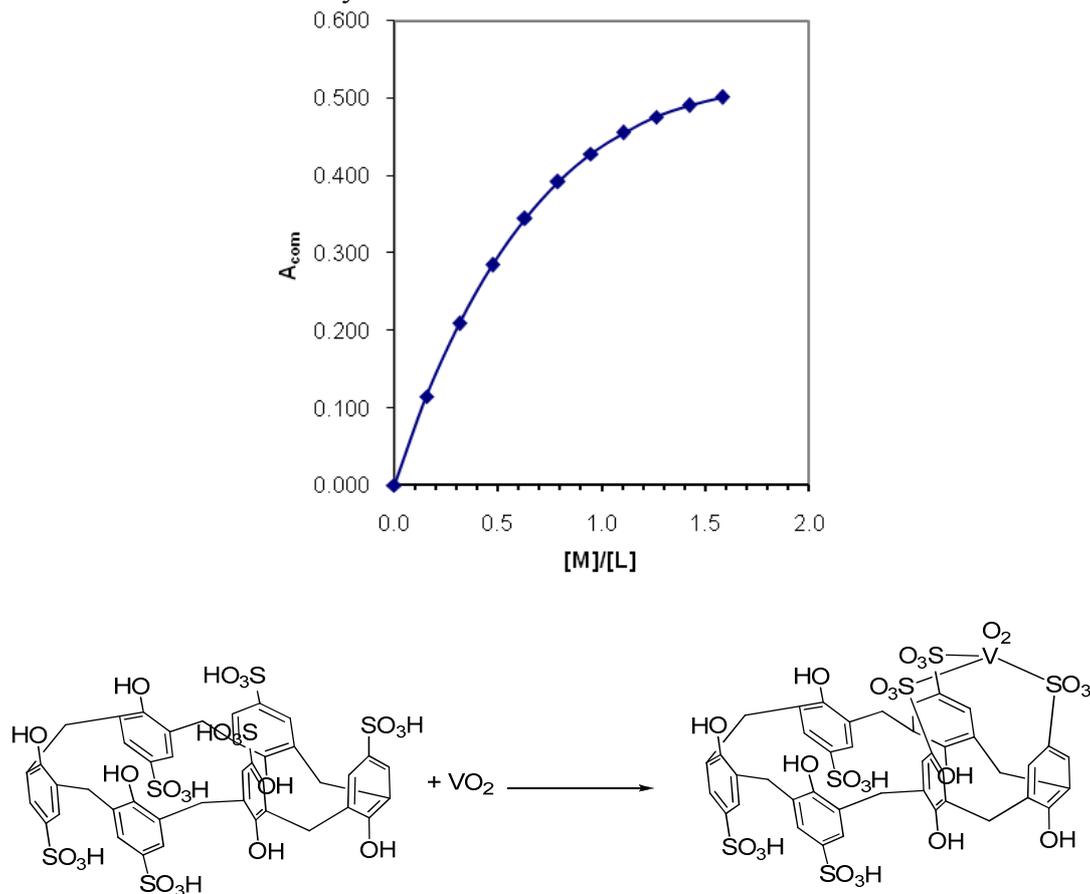


Fig. 3. Spectrophotometric titration plots, A_{com} complex versus the mole ratios of VO_2^+ to *p*-hexasulphonato-calix[6]arene at 25 °C, pH 1.7, and 285 nm.

Spectrophotometric titration plots, A complex versus the mole ratios of VO_2^+ to *p*-sulphonato-calix[6]arene at 25 °C, pH 1.7, and 290 nm.interactions with the SO_3H groups of the upper rim. It should be noted that one cannot interpret the present results by considering a binding of the cations used with the phenolic hydroxy groups of the lower rim. The interactions of this type have never been evidenced in acidic aqueous solution. Also, binding involves an important desolvation of cation and ligand which yields an unfavorable Gibbs free energy that should be compensated by the interactions taking place into the cavity. As expected, the affinity of the ligand is larger for the cation that is less strongly solvated. One of the most important parameters showing the nature of the intermolecular host-guest interaction is the enthalpy change of the reaction. This suggests a negative ΔH° and ΔS° in the case of VO_2^+ with *p*-hexasulphonato-calix[6]arene. The ΔH° and ΔS° values determined from the slope and the intercept of the nice straight line of $\ln K_s$ versus $1/T$ respectively and are listed in Table 2. The enthalpy change results from several factors including hydrogen bonding, electrostatic interactions, and Vanderwals forces. The entropy change also consists of several factors. In the entropy-driven reaction, the entropy gain is possibly due to the loss of the arrangement of water molecules originally surrounding the organic molecules that are in a highly ordered fashion. However, in the enthalpy-driven reaction, the entropy loss is possibly due to the freezing of motional freedom of the guest molecule as a result of the association with the host species. Average values of $\log K_s$ for *p*-hexasulphonato-calix[6]arene-dioxovanadium(V) at different temperatures together is reported in the Table 1.

Table 1. Average values of $\log K_s$ for *p*-hexasulphonato-calix[6]arene dioxovanadium(V) at different temperatures.

Temperature/°C	Cation	$\log K_s$
25	VO_2^+	3.46+0.04
30	VO_2^+	3.37+0.04
35	VO_2^+	3.29+0.02
40	VO_2^+	3.18+0.02

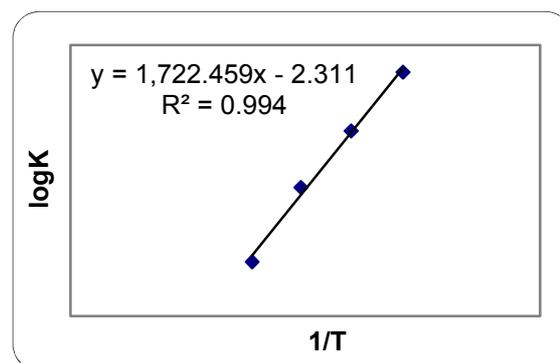


Fig. 4. The plot of $\log k$ versus $1/T$ for the binding of VO_2^+ to *p*-hexa sulphonato-calix[6]arene.

Table 2. Thermodynamic parameters (ΔG° , ΔH° , $T\Delta S^\circ$) for the binding of dioxovanadium(V) with *p*-hexasulphonato-calix[6]arene at 25 °C.

$\Delta G^\circ/\text{KJmol}^{-1}$	$\Delta H^\circ/\text{KJmol}^{-1}$	$T\Delta S^\circ/\text{KJmol}^{-1}$
8.58-	-14.270	-5.681

CONCLUSIONS

We have prepared complexive of *p*-sulphonato-calix[6]arene towards dioxovanadium(V) in acidic aqueous solution. Its demonstrated *p*-sulphonato-calix[6]arene properties are currently explored in separation studies involving dioxovanadium(V) of economical or environmental interest.

We concluded that, the molar ratio of ligand to metal was 1:1. The average amount of calculated formation constant was 3.46 at 25°. the more electric charge

effects on metal Vanadium(V) is the electrostatic force is stronger so the formed complex is stronger. We found also is no proton at pH=2 and negative charge is settled in lattice. There are six negative head and there are has five 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.

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