Equilibrium Constants of the Complexation of Molybdate Ion with para-Sulfonatocalix [4] arene in aqueous media

S. Z. Hashemizade[1*] and Ali Farajtabar[2]

[1] Department of Chemistr,y North Tehran Branch, Islamic Azad University, Tehran, Iran
[2] Department of Chemistry, Jouybar branch, Islamic Azad University, Jouybar, Iran

ABSTRACT

The complexation of sodium molybdate with para-sulfonatocalix [4] arene was studied in the temperature range from 20 to 40 ^{o}C and pH = 5.8 by spectroscopic method in water solution. The stability constants of complexes were calculated by the multiwavelength analysis of spectral data using SQUAD program. The equilibrium constant, spectroscopic data, molar absorptivities and concentrations of all species were adequately optimized by program when the chemical model with 1:1 stoichiometry was considered in the calculation. The extracted values of molar absorptivities and concentration profile of the formed complex were reported. The logarithms of the stability constants of complexes were calculated to be 3.672, 3.143, 2.986, 2.555, and 2.333 at20, 25, 30, 35and 40 ^{o}C respectively.

Keywords: P-sulphonato-calix [4] arene; Sodium molybdate; Equilibrium constant; Spectrophotometric method

INTRODUCTION

Calix[n]arenes together with cyclodextrins and crown ethers form an important group of macrocyclic receptors which have attracted much interest in various studies such as biological, analytical and supramolecular chemistry [1-3]. Calix[n]arenes easily synthesize from the condensation of formaldehyde with para-alkylphenols under alkaline conditions in which the number of phenolic ring bridged by methylene groups can be deliberately varied from 4 to 8 with the choice of synthetic routes. The chemical properties of calixarenes such as selectivity or solubility can be facility modified by the functionalization of both phenolic (lower rim) and para-aromatic faces (upper rim) [4]. Within calixarenes derivatives, para-sulfonatocalix[n]arenes, Fig. 1, have been the subject of numerous papers. This widespread interest is due to their biomedical application, high water solubility and similarities to biological systems [5-7]. Typically, the bioactivities of sulfonatocalixarenes including anti-viral, anti- bacterial, anti-thrombotic, enzyme inhibition and chloride ion channel blocking activities have received considerable attention in literature [2, 8-14].

One the most important properties of calix[n]arenes is their selective ability to accommodate metal ions. This aspect of calixarenes has found diversity application in the treatment of nuclear waste fluids, development of optical and electrochemical sensing devices and environmental safety

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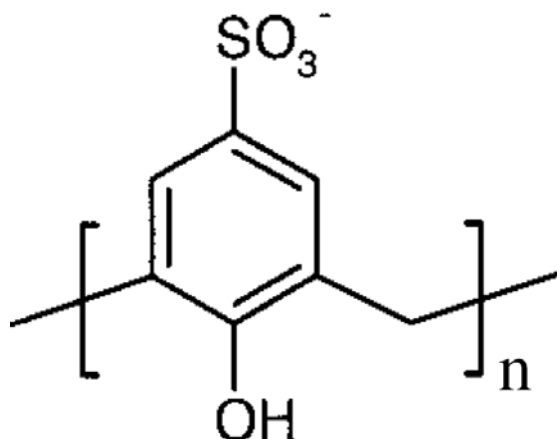
* Corresponding author: S.Z. Hashemizade

Fig. 1. Molecular structure of para-sulfonatocalix[n]arenes.

[15-23]. The binding properties of para-sulfonatocalix [4] arenes towards some mono-, di- and trivalent metal cations have been studied by different methods [24-32]. Results showed that multivalent metal ions form outer-sphere complexes through electrostatic interactions with the four SO_3^- groups on the upper rim of para-sulfonatocalix [4] arenes. On the other hand, monovalent cations are folded within the cavity and bound with the aromatic rings of the calixarene by -cation interaction.

In the present work, we report the results of spectroscopic study on the complex affinity of para-sulfonatocalix[4]arenes toward MoO_4^{2-} ion in the temperature range from 20 to 40 ^{o}C and pH = 5.8 in aqueous media and The values of ΔH° and ΔS° were calculated .

EXPERIMENTAL
Para-sulfonatocalix [4] arene was purchased from Acros Organics. Sodium molybdate was obtained from Merck and used without further purification. All dilute solutions were prepared from double distilled water with a specific conductance equal to 0.5 ± 0.1 μScm^{-1}. The pH of solutions was adjusted by diluted solutions of NaOH and HCl.

A Jenway research pH-meter (model 827) was used for the pH measurements. The hydrogen ion concentration was measured by Metrohm pH-meter which was calibrated with pH 4.0 and 7.0 buffers in aqueous solutions.

Absorption spectral measurements were taken on a UV-Vis Cary 300 scanning spectrophotometer equipped with a Pentium 4 computer using 10 mm quartz cells. The temperature of system was thermostated at desired temperature by circulating water from an isothermal bath. In preparation of all experimental solutions, appropriate amount of diluted NaOH or HCl solution were used to adjust pH value at 5.8. In spectroscopic titration, a 2.5 mL solution of para-sulphonato calix [4] arene, 9.90×10^{-4} mol L^{-1}, was transferred to 4 mL quartz cuvette and then titrated with stepwise addition of a molybdate ion solution 1.97×10^{-3} mol L^{-1}. After each addition of metal ion solution, the spectral changes of calixarene were recorded at 1 nm intervals in wavelength range from 260 to 295 nm. The spectral data were transferred into excel format for further mathematical analysis. Data manipulation were performed in Microsoft excel environment to construct date matrices for input files. Equilibrium constant calculation was done by SQUAD program [33-35].

RESULTS AND DISCUSSION
The recorded absorption spectra of para-sulfonatocalix [4] arene in different metal

ion concentrations at 25 $^{\circ}$C are shown in Fig. 2. It is clear that the absorption spectral changes of calixarene are attributed to the formation of complex species by coordination with metal ion. Assuming that the complex M_pL_q formed is characterized by its stoichiometry, p and q, where M and L represent metal ion and the calix, respectively. To determine the stability constant of complexation, K_s, equation 1 is defined,

$$qM + pL \rightleftharpoons M_qL_p$$
$$K_s = [M_qL_p]/([M]^q[L]^p) \qquad (1)$$
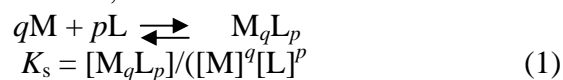
and the mass balance equations can be shown as follows:

$$[M]_0 = [M] + q[M_qL_p] \qquad (2)$$
$$[L]_0 = [L] + p[M_qL_p] \qquad (3)$$

The total concentration of metal and calix at each titration point was represented by $[M]_o$ and $[L]_o$ respectively.

In solution, containing metal ion, calixarene and complex species, a recorded absorbance A_j at wavelength j can be written by

$$A_j = [L]\varepsilon_{Lj} + [M]\varepsilon_{Mj} + [M_qL_p]\varepsilon_{Cj} \qquad (4)$$

Where ε_{Lj}, ε_{Mj} and ε_{Cj} are molar absorptivities of calix, metal ion and complex at the jth wavelength respectively. For equilibrium constant calculation, initial absorbance data can be introduce into a matrix **R** in which Aij is element of this matrix measured at the jth wavelength for the ith titration point.

Therefore we designate m absorption spectra that will be measured at n wavelengths in a $m \times n$ matrix **R**; the m spectra form the rows of **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, **R** can be decomposed into the product of a concentration matrix **C** ($m \times N$) and a matrix of the molar absorptivities **S** ($N \times n$).
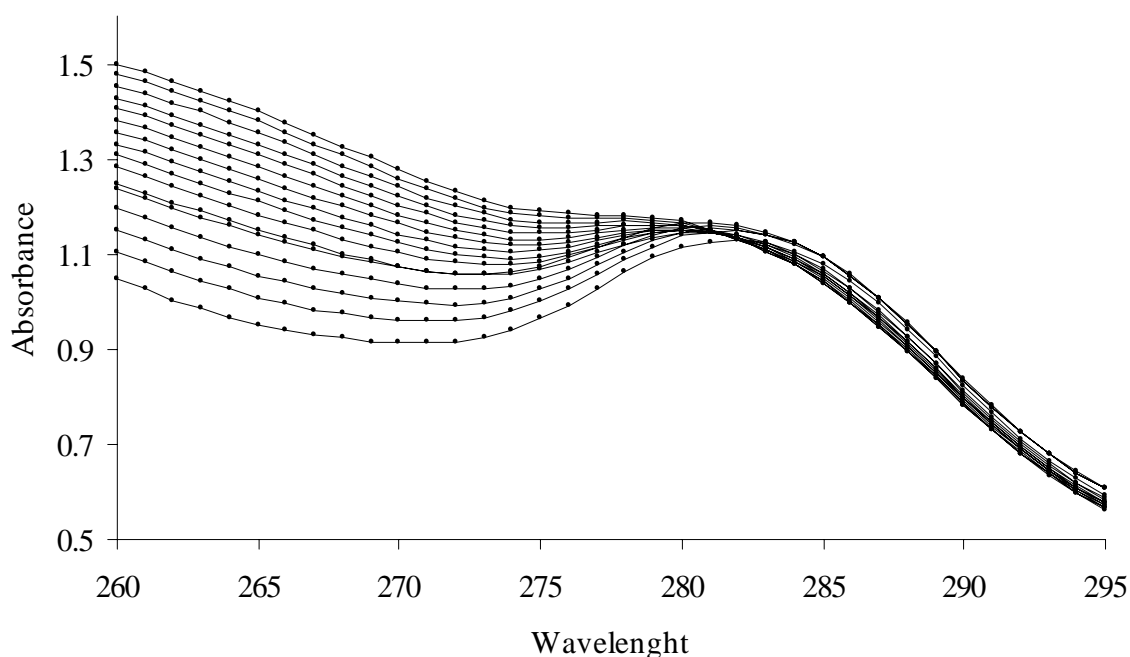
Fig. 2. Spectral changes of para-sulfonatocalix[n]arenes (9.90×10^{-4} mol L^{-1}) in different metal ion concentration at 25 ^{0}C.

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However, because of the inherent noise in the measured data, the decomposition does not represent **R** exactly. The matrix **T** of the residuals is given by the difference between **CS** and **R**

$$T = CS - R \qquad (5)$$

In the fitting procedure, those matrices **C** and **S** are determined which best represent the original matrix **R**. The task of the fitting procedure is to optimize the matrix **T** of the residuals, equation 5, according to the least-squares criterion. A multiwavelenght spectral analyzing program such as SQUAD can be used to adjust values of K_S and molar absorptivities through minimizing the matrix **T** of the residuals.

To find stoichiometric coefficient of complex, different chemical models with different species were supplied in the input file. For each chemical model, equilibrium constant was refined by the nonlinear regression algorithm and at the same time concentration profiles of all species together with a matrix of molar absorptivities were simulated. The residuals analyses were performed to identify which chemical model represents experimental data adequately. The physical meaning of estimated molar absorptivities and stoichiometric indices has to be considered. The stoichiometric indices should be integer number. Also negative value for molar absorptivities cannot be

acceptable. For the optimum calculation, standard deviations of all parameters will be lowest.

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. The model finally chosen, formed by ML, resulted in a satisfactory numerical fitting for the obtained experimental data.

Results of the logarithm of equilibrium constant for interaction of molybdenum ion with para-sulfonatocalix [4] arene at different temperature and constant pH of 5.8 were shown in table 1. Convergence was achieved in range of 3 to 7 cycles. The standard deviation in the absorbance data was calculated to be low. The computed molar absorptivities of species at 25 °C were shown in Fig. 3. independence of wavelength.

The concentration of the complex species was calculated according to the refined stability constant at 25 °C and its distribution diagram was depicted in Fig. 4.

Table 1. The logarithms of equilibrium constant for interaction of molybdenum ion with para-sulfonatocalix [4] arene at different temperatures

| Temperature / °C	logK	Standard Deviation
20	3.672	0.015
25	3.143	0.013
30	2.986	0.016
35	2.555	0.012
40	2.333	0.013
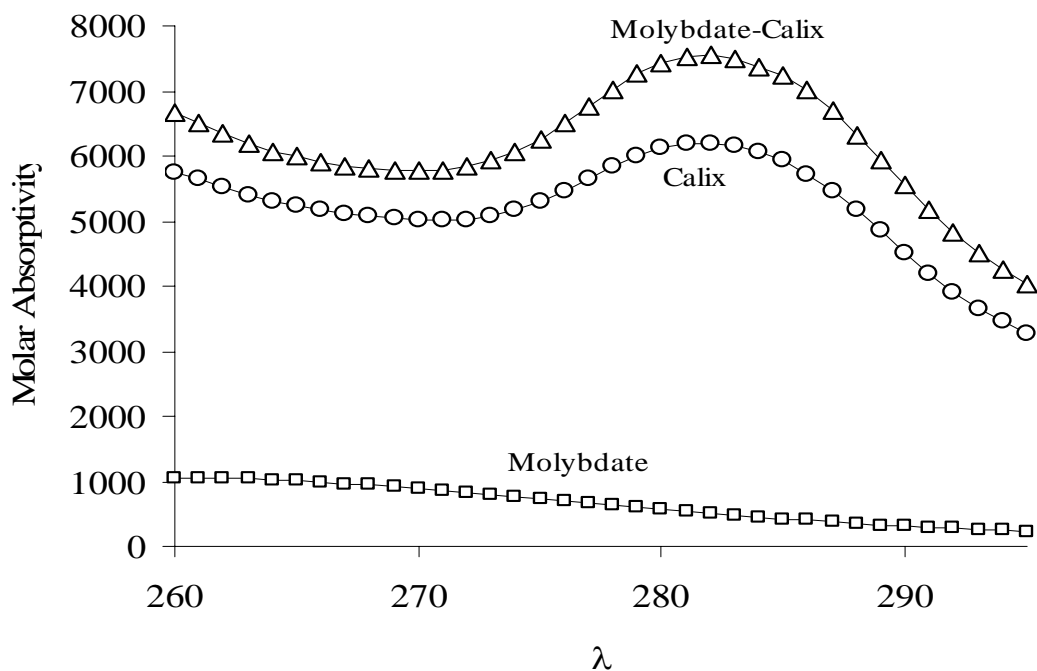
Fig. 3. Computed molar absorptivities of molybdenum (□), para-sulfonatocalix [4] arene (○) and complex specie (Δ) versus absorbance wavelength at 25 °C.
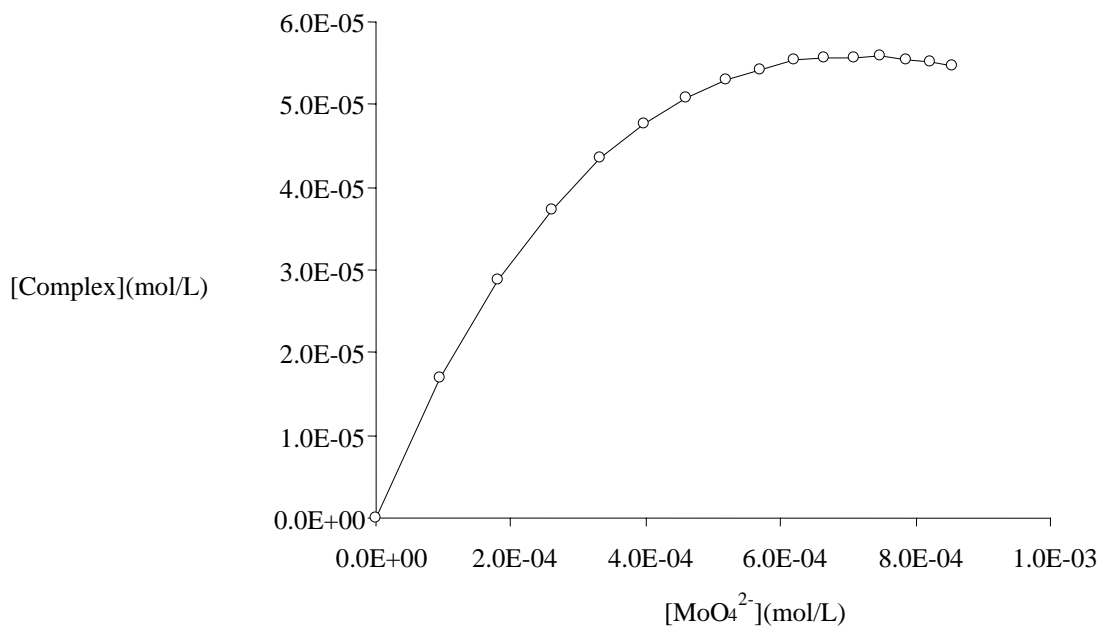
Fig. 4. Concentration profile of complex species at each titration point obtained by SQUAD program at 25 °C.

As shown in Fig. 5, the plot of logK versus 1/T for this complexation exhibits a straight line where the magnitude of change in the enthalpy and entropy can be determined from the slope and the intercept. The values of $\Delta H°$ and $\Delta S°$ were calculated to be -115.04 kJ.mol^{-1} and -323.415 J.mol^{-1}.K^{-1} respectively.
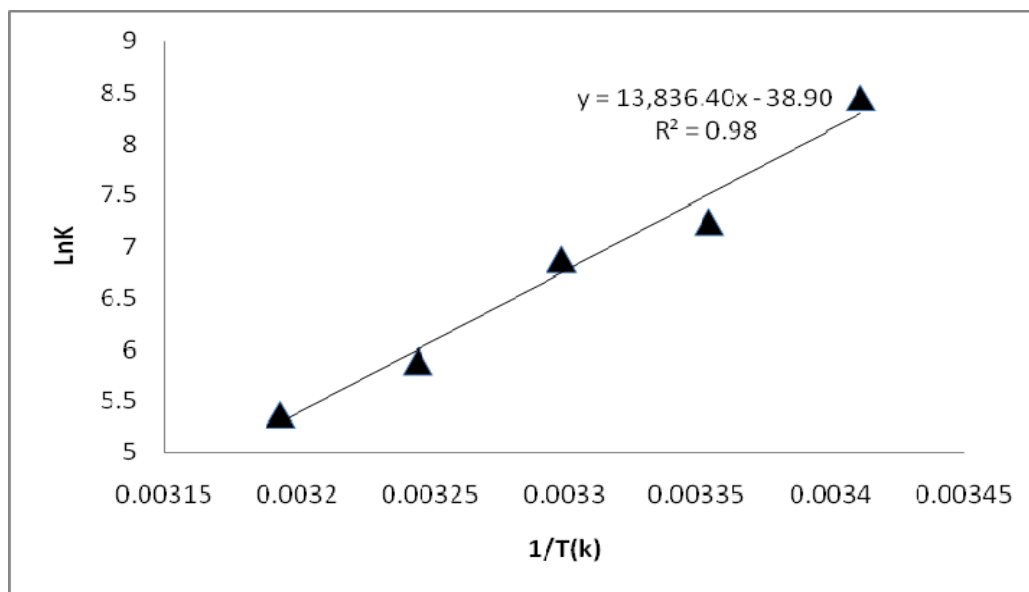
Fig. 5. The plot of logK versus 1/T for interaction of molybdenum ion with para-sulfonatocalix [4] arene.

Table 2. Thermodynamic parameters (ΔG°, ΔH°, ΔS°) for the binding molybdenum ion with p-sulphonato-calix [4] arene at 25 °C

$\Delta G^O/kJ.mol^{-1}$)	$\Delta H^O/kJ.mol^{-1}$)	$T\Delta S^O/kJ.mol^{-1}$)
-17.99	-115.04	-96.37

It was shown that the complexes formed between metal ion and para-sulfonatocalix[n] arenes are charge dependent [16]. As revealed by different groups, the multivalent metal cations complexes are formed by strong electrostatic interaction with sulfonate groups of calixarene. Their complex reactions are mainly controlled by positive entropy change [17, 25]. In contrast with multivalent cationic ions, the complexation processes for the monovalent metal cations are totally enthalpy controlled with the negative enthalpy and entropy function changes.

The binding abilities are attributed to the interactions between the metal and the π-electrons of the calixarene cavity [27-79]. The thermodynamics parameters obtained from this study may be led to the conclusion that the complexation interaction is metal-π-electrons type. The interaction of molybdenum (VI) ion with upper rim SO_3^- groups of calixarene should be unacceptable due to their repulsive electrostatic interaction with metal ion. However these results suggest that the complex binding strength may be increased through the hydrogen bonding interactions between oxo groups of molybdenum (VI) ion and four hydroxyl groups on the lower rim of para-sulfonatocalix [4] arene similar to obtained for the uranyl ion [4].

CONCLUSIONS
The equilibrium constant for interaction of sodium molybdate with para-sulfonatocalix [4] arene was successfully determined by SQUAD program based on the multiwavelenght analysis method. The results indicate that the value of logK was 3.672, 3.143, 2.986, 2.555, and 2.333 at 20, 25, 30, 35and 40 °C respectively. The

optimized spectral data have also successfully been utilized in calculation of molar absorptivities and concentrations profile of all species involved in complexation reaction. It seems that the complex may be formed through the hydrogen bonding interactions between molybdenum (VI) ion and hydroxyl groups on the lower rim of calix [4] arene.

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