Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 8 (2) 135-139: Summer 2011
(J. Phys. Theor. Chem. IAU Iran)
ISSN 1735-2126

Complexation of L-arginine and L-lysine by *p*-sulphonatocalix [6] arene in aqueous solution at different temperatures

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Received August 2011; Accepted September 2011

ABSTRACT

The interaction of *p*-sulphonatocalix [6] arene towards L-arginine and L-lysine has been studied in acidic aqueous solution (pH 2) using UV-Vis spectrophotometric titration technique. The *p*-sulphonatocalix [6] arene was found to be able to form 1:1 complexe with amino acids in water. The values of the association constant were determined at different temperatures to evaluate the thermodynamic functions of the complexation reaction. The thermodynamics values of complexes were compared to each other.

Keywords: *p*-sulphonatocalix [6] arene; Amino acid; Equilibrium constant; Thermodynamic parameters

INTRODUCTION

Calixarenes and their derivatives are one of the three major groups of macrocyclic compounds able to enter into selective complexation with neutral or ionic species in supramolecular chemistry [1]. The p-sulfonatocalixarenes have attracted considerable attention in host-quest chemistry because of their high solubility in water, less toxic than other host molecules and similarity to biological functions [2]. They are composed of phenol units connected by ortho-methelene [3]. The interaction of p-sulfonatocalixarenes with different bioactive molecules such as protein, is an interesting topic in biological and pharmaceutical fields [4]. The interactions of p-sulfonatocalixarenes with amino acids can provide useful information on the mechanism of the binding of p-sulfonatocalixarenes to these bioactive molecules. In recent decay, the interactions of p-sulfonatocalix [6] arenes with amino acids and peptides have been studied by NMR, calorimetry and HPLC [5-10]. These studies show that the complexes were often formed with 1:1 stoichiometry in water through various interactions such as electrostatic, hydrophobic, hydrogen bonds and π–π interactions. NMR studies confirm that aliphatic and aromatic chains of amino acids are inserted into the cavity of p-sulfonatocalixarenes. The complexation process has been shown that is mainly controlled by the favourable enthalpy however the favorable entropy resulting from the desolvation of the charged groups upon ionic interaction also plays an important role.

In this research, the interactions of p-sulphonato calix [6] arene towards L-arginine and L-lysine have been studied in acidic aqueous solution at different temperatures. The effect of temperature and thermodynamic functions of complexation were studied to elucidate the possible mechanism for the formation reaction.

EXPERIMENTAL

Chemicals

25, 26, 27, 28-tetrahydroxy-5, 11, 17, 23-tetrasulphonic calix [6] arene hexahydrate was obtained from Acros Organics, L-arginine and

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L-lysine were purchased from Aldrich and used without further purification. All dilute solutions were prepared from double distilled water with a specific conductance equal to 1.2 ± 0.1 μScm^{-1}.

Measurements

A Jenway research pH-meter (model 3520) 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 $\pm$ 0.001 pH units.

Spectrophotometric measurements were performed using a UV-Vis Shimadzu 2100 scanning spectrophotometer with a Pentium 4 computer using 10 mm quartz cells. The system was thermostated at constant temperature by circulating water from an isothermal bath. For each experiment, a 2.5 mL solution of *p*-sulphonato calix [6] arene, 9.90×10^{-4} mol dm^{-3}, was titrated with stepwise addition of an amino acid solution 2.45×10^{-2} mol dm^{-3} both of the same pH 2 in the different temperatures (20 – 35 °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 amino acid solution, the absorbance was measured in the range 250-350 nm (in the interval of 1 nm) and the procedure extended up when the ratio of amino acid to the calix concentrations reaches to 2.5. The UV-Vis spectra of the mixtures undergo small changes but the measured absorbance was sufficient to allow the treatment of the data with the computer program. 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.

RESULTS AND DISCUSSION

Assuming that the absorbance of the calix would change upon complexation with an amino acid, we performed spectrophotometric measurements. The complex A_pC_q formed is characterized by its stoichiometry, p and q, where A and C represent an amino acid and the calix, respectively. To determine the formation constant of complexation, K_S, Eq. 1 is defined,

$$qA + pC \;\; A_qC_p \;\; K_s = [A_qC_p]/([A]^q[C]^p) \quad (1)$$

Determination of the formation constant was employed using the method described before [11-17]. Absorbance, A, was measured by successive addition of an amino acid solution to the calix solution (see experimental section). Typically as shown in Fig. 1, the absorption bands of the calix change upon addition of each amino acid solution in all cases. Treatment of the spectrophotometric data obtained during the titrations was conducted with the computer program Squad [18-20].

The stoichiometric formation constants were computed from the data using the computer program. The number of experimental points were more than 40 (maximum 50) for each titration. 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 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** ($N \times n$). 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**

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

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, 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 nonlinear least-squares fitting to find the set of parameters that result in a minimum of U.

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

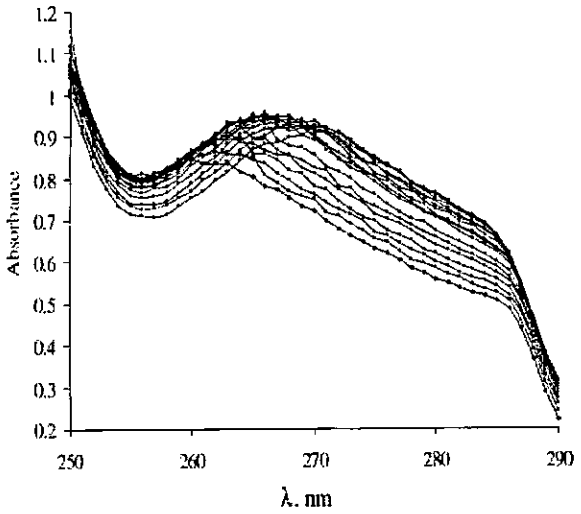

Fig. 1. Spectral changes of *p*-sulphonato calix [6] arene upon addition of L-arginine solution at pH 2 and 25 °C.

Different chemical models with different stoichiometry 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 can not 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 AC, resulted in a satisfactory numerical and graphical fitting for the both systems. Fig. 2 is shown as a typical example of the degree of fit test for the observed and calculated absorbances data at 25 °C and 294 nm.

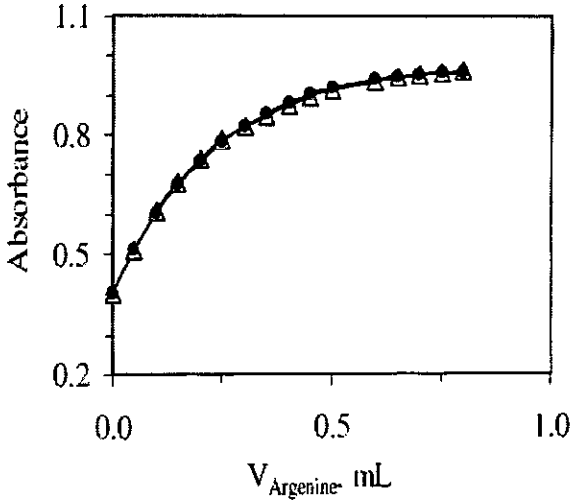

Fig. 2. The degree of fit test for the observed (Δ) and calculated (•) absorbances data for *p*-sulphonato calix [6] arene + L-arginine at 25 °C and 294 nm.

The logarithms of equilibrium constants of the 1:1 complex species are listed in Table 1 at different temperatures.

Table 1 shows that the values of equilibrium constants decrease on increasing the temperature. In Fig. 3, we have plotted logKs versus 1/T for these complexations. The values of ΔH° and ΔS° were determined from the slope and the intercept of the graph and listed in Table 2.

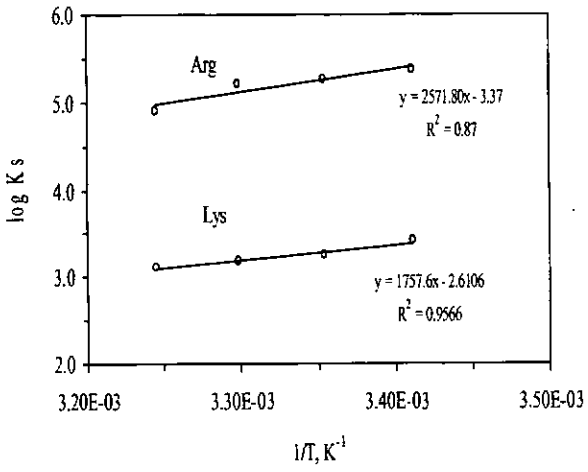

Fig. 3. The plot of logKs versus 1/T for the binding of the *p*-sulphonato calix [6] arene with L-arginine and L-lysine at pH 2.

Table 1. Average values of logKs for interaction of *p*-sulphonato calix [6] arene towards L- arginine and L-lysine at different temperatures

temperature / °C	logKs (L-lysine)	logKs (L-argenine)
20	3.41	5.37
25	3.25	5.26
30	3.18	5.21
35	3.11	4.91

Table 2. Thermodynamic functions for the reaction between L-arginine and L-lysine with *p*-sulphonato calix [6] arene

L-argenine		L-lysine	
$\Delta H°$ /kJmol^{-1}	$\Delta S°$ /Jmol^{-1}	$\Delta H°$ /kJmol^{-1}	$\Delta S°$ /Jmol^{-1}
-49.24	-64.53	-33.65	-49.98

These results show that the complexations of p-sulphonatocalix [6] arene with L-arginine and L-lysine are driven by the favorable negative enthalpy changes which are originated from several factors including hydrogen bonding, electrostatic interactions, and Van Der Waals forces. The values of equilibrium constants indicate that, in acidic solution, the interactions between p-sulphonatocalix [6] arene and L-argenine are stronger than those with L-lysine. The SO_3^- groups of p-sulphonatocalix [6] arene are completely deprotonated at pH = 2 however the phenolic hydroxyl groups on the upper rim of calix are undissociated. At the pH = 2, L-argenine and L-lysine possess two positive ammonium binding site. Therefore the complex formation of p-sulphonatocalix [6] arene with L-argenine and L-lysine can be attributed to the electrostatic interaction of positively charged amino acids with negatively sulfonic sites of calix.

Conclusion

The complexation of L-argenine and L-lysine by p-sulphonatocalix [6] arene have been investigated by UV-Vis spectrophotometric titration at pH = 2 and different temperatures. The equilibrium constants, enthalpy and entropy changes of complexation were determined. The complexation interaction is favored by enthalpic contributions and seems to be mainly attributed to electrostatic interactions.

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