Complexation of Tri-o-Propoyl-p-t-Butyl Calix[4]Arene with Alkali Metal Cations in Carbon Tetrachloride Solvent

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ABSTRACT.

The complexive abilities of tri-o-propyl-p-tert-butyl-calix[4]arene towards alkali metal ions Li^+, Na^+, K^+, Rb^+, and Cs^+ in carbon tetrachloride have been evaluated at 25 °C, using UV-vis spectrophotometric techniques. The results showed that the ligand is capable to complex all alkali cations by a 1:1 metal to ligand ratio. The selectivity presented considering the calculated stability constants is in the order $Na^+ > Cs^+ > Li^+ > K^+ > Rb^+$.

INTRODUCTION

Calix[n]arenes are a very fascinating class of container molecules and their abilities towards ion or molecule recognition were studied extensively among the past decade. They are cyclic oligomers which are formed by condensation reaction of formaldehyde and para-substituted phenol derivatives /1/. Calixarenes are basket-shaped compounds with potential interest for host-guest complexation. Functionalization at the lower rim may lead to design and synthesis of the ligands suitable for various metal complexation /2/. The control of cation-binding ability of calixarenes has been the subject of more recent investigations. A quantitative measure of the interaction strength between the two chemical species (macrocycle and guest) in the given solvent is provided by the stability constant and the conformation of both uncomplexed and complexed species appears to be a distorted cone. The focus has been on the introduction of donor groups onto the calixarene framework for controlling their complexation phenomena. The ability of calixarene systems to interact with alkali metal ions has long been recognized and has led to several ionophores increasingly selective for a specific cation. A variety of optical methods for the detection of cations in solution are well established and have been extensively reviewed /3-9/. One of the successful approaches is using spectrophotometic properties of calixarenes. These compounds show UV absorption bands at around 270-290 nm due to the electronic transitions in the phenol groups. For photometric diagnosis of an ion or

mm quartz cells. In all cases, the procedure was repeated at least three times and the resulting average values and corresponding standard deviations are shown in the text and Tables.

Procedure

2.5 cm^3 solution of the ligand (1.98×10^{-4} mol dm^{-3}) was titrated with stepwise addition of an alkali cation solution (1.61×10^{-3}, 1.75×10^{-3}, 1.61×10^{-3}, 1.59×10^{-3}, and 1.63×10^{-3} mol dm^{-3} for Li, Na, K, Rb, and Cs, respectively), both in carbon tetrachloride solution, the UV-vis spectrum of the mixture undergoes small changes at 280-290 nm. However, the absorbance changes were sufficient to allow the treatment of the data by the computer program /11/.

RESULTS AND DISCUSSION

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

$$pM + qL + M_pL_q \qquad K_S = [M_pL_q] / [M]^p[L]^q \tag{1}$$

The method of determination of formation constant has been described before /12-15/. The absorbance, A, was measured for solutions, as described in the experimental section, and the corrected absorbances for unreacted ligand and each metal ion are shown in Table 1. For calculating the formation constants, the spectrophotometric titration data were analysed at a wavelength in UV range that is given by

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

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

$$[\text{metal ion}] = C_M - [\text{complex}] \tag{3}$$

$$[L] = C_L - [\text{complex}] \tag{4}$$

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

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

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 /11/, 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,

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

where a_i is a quasi-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 the calculated values.

It was checked for other proposed species existing in significant concentration over a reasonable range of data. As expected, polynuclear complexes were systematically rejected by the computer program, as also M_2L and ML_2. The model finally chosen, formed by ML, resulted in a satisfactory numerical and graphical fitting. The average values of the formation constants for the 1:1 complexes of L + each metal ion for various wavelengths are listed in Table 2.

The interesting curve resulting from the spectrophotometric titration of the ligand by Na^+ and Cs^+, Figure 2, shows a sharp break point when the ratio of concentrations of metal ions to the ligand reaches unity, indicating the formation of stable complexes for Na^+ and Cs^+. The same titration for Rb^+ shows the absorbance increase within a very small range and no significant break in complexation curve, indicating low stability constant of formation. However, the spectrophotometic titration curve of the ligand by Li^+ and K^+ displays a more continuous variation in the absorbance with concentration ratio. In this case, extrapolating the slopes at high and low metal to ligand ratios gives intersection points which correspond to 1:1 complex stoichiometry. This behaviour indicates a typical less stable complex than the one found for Na^+.

The main objective of this study was to estimate alkali metal ion binding selectivities based on stability constants of the formed complexes. The proposed calixarene in this work (Figure 1) consists of four aromatic rings with two different lower rim substitutions. In general, calixarenes have two different sites of complexation: endo and exo /16-19/. In exo complexes, phenolic oxygens are capable of hard electrostatic interactions with small hard cations, such as Li^+ [20] and Na^+ /21,22/, while the phenyl π-electrons participate in endo complexes with soft dispersion and induction interaction with large soft cations, such as Cs^+ /23/. Under this condition rubidium cation is too large to form stable exo complexes and too small to have enough polarizability to form endo complexes. The solid-state NMR analysis of alkali metal cations series confirms this behaviour /24/. The result obtained in this work shows a preference for Na^+ complexation over K^+ or Li^+ complexations, suggesting the above speculation.

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