A Thermodynamic Study of the Association of K^+ and Rb^+ Cations with 1,3-Bis(benzyloxy)-*p-tert*-butylcalix[4]crown-5 in a $CHCl_3$–Methanol Mixture

Shehadeh A. Mizyed[a] and Muhammad Ashram[b]

[a] Chemistry Department, Yarmouk University, Irbid, Jordan
[b] Chemistry Department, Mu'Tah University, Al-Karak, Jordan

Reprint requests to Dr. S. A. M.; E-mail: z79sam@hotmail.com

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Dedicated to Prof. Paris E. Georghiou on the occasion of his 59th birthday.

The conductivity during the complexation reaction between K^+ or Rb^+ and 1,3-bis(benzyloxy)-*p-tert*-butylcalix[4]crown-5 in a $CHCl_3$-methanol mixture at 288 – 303 K has been measured. The conductivity data were analyzed using a computer program based on 1 : 1 stoichiometry. The stability constants of the resulting complexes were determined, indicating that K^+ is more stable than Rb^+ in the solvents used. The ΔH and ΔS values for the complexation processes were determined from the temperature dependence of the complexation constants. Their significance as well as the solvent effect is discussed.

Key words: Calix[4]crown-5; Complexation; Conductivity; Thermodynamics.

1. Introduction

Calixarenes and their derivatives are known to form complexes with a wide variety of neutral, cationic and anionic guests [1]. Calixarenes are cyclic oligomers formed by the base-catalyzed condensation of formaldehyde and *p-tert*-butylphenol [2]. They can be modified at two main sites: at the "lower rim" and/or at the "upper rim" [3]. The aim of these chemical modifications is: (i) to enhance the selectivity and efficiency of their complexation properties, (ii) to control their conformations and (iii) to enhance their solubilities [4]. There are many instances of lower rim functionalization to form, for example, esters, ketones [5], amides and calixcrowns [2, 6].

Calixcrowns are macromolecular hybrids composed of calix[*n*]arenes and crown ethers. They are very effective complexing agents for alkali and other metal ions [7]. Calix[4]crown [8] which contains a single crown ether strap (mono-bridged) or a double crown ether strap (bis-bridged) has been constructed from calix[4]arene. It was found that the mono-bridged calix[4]crown form 1 : 1 complexes with metal cations, while the bis-bridged calixcrowns are generally able to form 2 : 1 complexes [7]. Calix[6]crowns and calix[8]crowns were also prepared [8]. Calixcrowns with different crown ether moieties were prepared; calix[4]crown-6 was prepared and extensively investigated in the complexation with alkali metal cations, in particular Cs^+. Calix[4]crown-5 was also prepared, but less results were reported about its complexation.

The complexation of metal cations with cyclic oligomers is a continuously growing branch of host-guest chemistry. Several different experimental techniques have been applied for studying the formation of such complexes.

Spectrophotometry [5], potentiometry, NMR spectroscopy, calorimetry, and to a very small extent, conductometry have been mainly used to determine the stability constants and the thermodynamic parameters of the complexation between calixarene derivatives and metal cations [6]. The scarcity of comparative studies concerning the association of alkali cations with calixcrowns by using conductometry has motivated us to carry out the present study.

In this study the stability constants of the complexes of calix[4]crown-5 with both K^+ and Rb^+ ions were determined at different temperatures in $CHCl_3$-methanol solution by using conductometry as well as the thermodynamic parameters.

2. Experimental

1,3-Bis(benzyloxy)-*p*-*tert*-butylcalix[4]crown-5 (**1**) was prepared according to [9]. Methanol and $CHCl_3$ (HPLC grade, Scharlau, assay 99.6%) were used after fractional distillation. Conductivities of methanol and $CHCl_3$ were less than 2.0×10^{-7} S cm^{-1} and almost S cm^{-1}, respectively. The salts KCl (Aldrich, 99%) and RbCl (Aldrich, 99%) were dried under vacuum at 70 °C prior to use. Solutions of KCl and RbCl with concentrations of ca. 1.0 to 1.1×10^{-4} M were used. These solutions were also used as solvents for preparing the calixcrowns solutions. Known amounts of calixcrowns solution $(1.0-2.0) \times 10^{-3}$ M was used. The ionic strength is kept constant, since the complexation does not change the charges of the species. Three runs were used for the calculation of a certain K value. The stability constants were evaluated at various temperatures by using a computer program based on the simplex algorithm of Nedler and Mead [10]. Other details concerning equipment and techniques were similar to those reported in [7].

3. Mathematical Treatment

The stoichiometry of the binding of alkali cations with calixcrown of the type studied in this study is 1 : 1 in dilute solution [8]. Consequently, the binding of an alkali cation, M^+, by a calixcrown, L, can be represented by the equilibrium

$$M^+ + L \leftrightarrows ML^+ \tag{1}$$

with

$$K = \{[ML^+]/[M^+][L]\} \times \{f[ML^+]/f[M^+]f[L]\}, \tag{2}$$

where $[ML^+]$, $[M^+]$, $[L]$ stand for the equilibrium concentrations (M) of the 1 : 1 complex, uncomplexed cation, uncomplexed calixcrowns and f for the activity coefficient of the species, respectively. Under the dilute conditions used in the present study, it is argued [11] that the factor involving the activity coefficients of the uncharged ligand, $f[L]$, in (2) can reasonably be assumed to be unity and $f[ML^+] \approx f[M^+]$. Thus, the activity coefficients cancel and therefore the stability constants reported in the present study are essentially thermodynamic constants.

If α is the fraction of the total metal ion that is uncomplexed with the ligand, then the following equations result:

$$[M^+] = \alpha[M^+]_t, \tag{3}$$

$$[ML^+] = (1-\alpha)[M^+]_t, \tag{4}$$

$$[L] = [L]_t - (1-\alpha)[M^+]_t, \tag{5}$$

where $[M]_t$, $[L]_t$ are the total concentrations (M) of the cation and ligand. The molar conductivities Λ can be calculated using the equation

$$\Lambda = 10^3\kappa/[M]_t, \tag{6}$$

where κ is the conductivity of the test solution in S cm^{-1}. On the other hand, Λ can be related to α by the following equation:

$$\Lambda = \alpha\Lambda_m + (1-\alpha)\Lambda_c, \tag{7}$$

where Λ_m is the molar conductance of the uncomplexed metal (MCl) before addition of the ligand, and Λ_c is the molar conductance of the complexed (MLCl) salts, respectively. (7) is an approximate expression which states that Λ is calculated by the simple additivity rule applied to two electrolytes (complexed and uncomplexed salt) with a common anion at a constant ionic strength [12]. In (7), Λ is treated as a calculated quantity in the simplex program, while K and Λ_c are adjustable parameters. The reported values of K and Λ_c correspond to the condition that $\Sigma(\Lambda - \Lambda_{cal})^2$ is a minimum, at which the program terminates. Other details were reported in [13]. The values of $\log K$ obtained in this study are given in Table 1 together with relevant literature values and the thermodynamic parameters.

4. Results and Discussion

Figure 1 illustrates the behavior of Λ as a function of the ratio $[L]_t/[M^+]_t$, where $[L]_t$ denotes the total molar concentration of calixcrown **1** (Fig. 2) in the test solution, and $[M^+]_t$ denotes the concentration of $RbCl^+$ at different temperatures. Figure 1 shows that the observed conductance of the test solutions decreased and leveled out near 1 : 1 mole ratio indicating the formation of an 1 : 1 complex. The decrease in the observed conductance is due to complex formation. This is expected due to the size increase of the cation in moving from the free to the complex state that results in decrease of the cation mobility. Factors related to the changes in the viscosity of the test solution caused by the presence of a macrocycle, were discussed in similar studies and found to be of no major concern [14].

The values of $\log K$ obtained in the present study for calixcrown-5 complexes with K^+ and Rb^+ at 25 °C in different non-aqueous solvents are given in Table 1.

Table 1. Values of log*K*, $\Delta H°$, $\Delta S°$ and $\Delta G°$ for the 1 : 1 complexes of K$^+$ and Rb$^+$ 1,3-bis(benzyloxy)-*p*-*tert*-butylcalix[4]crown-5 in a CHCl$_3$-methanol mixture at 25 °C.

Cation	Medium* (% CHCl$_3$:MeOH)	Method	log*K* (M^{-1})	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/K mol)	$\Delta G°$ (kJ/mol)
K$^+$	40 : 60	Cond.[a]	5.18 ± 0.06			
	50 : 50	Cond.[a]	5.40 ± 0.10	−49.9 ± 0.5	−65.5 ± 0.3	−30.4
	60 : 40	Cond.[a]	5.25 ± 0.09			
	CDCl$_3$: H$_2$O[b]	Extr.[c]	6.08		−34.3	
Rb$^+$	40 : 60	Cond.	4.18 ± 0.07			
	50 : 50	Cond.[a]	4.40 ± 0.11	−10.2 ± 0.3	50.6 ± 0.5	−25.3
	60 : 40	Cond.[a]	4.46 ± 0.10			
	CDCl$_3$: H$_2$O[b]	Extr.[c]	4.77			−26.8

* % of volume. [a] Conductivity. [b] Data from [9]. [c] Extraction.

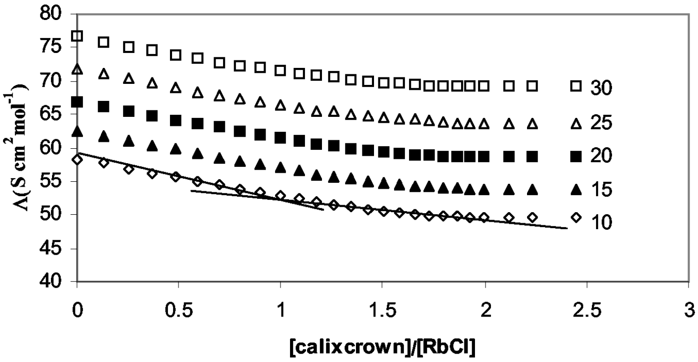
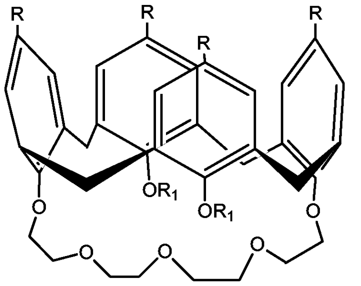


Fig. 1. Plot of the molar conductivity, Λ, vs. mole ratio $[L]_t/[M^+]_t$ for the binding of Rb$^+$ (1.5572e-4 M) by **1** in a (1 : 1) CHCl$_3$-methanol mixture at different temperatures (in °C).



1 R = *tert*-butyl, R$_1$ = CH$_2$C$_6$H$_5$

2 R = H, R$_1$ = CH$_3$

3 R = *tert*-butyl, R$_1$ = CH$_2$CH$_3$

Fig. 2. Structures of 1,3-Bis(benzyloxy)-*p*-*tert*-butylcalix[4]crown-5 (**1**), 1,3-dimethoxy-calixcrown-5 (**2**) and 1,3-diethoxy-*p*-*tert*-butylcalix[4]arene crown-5 (**3**).

The results indicate that the stability of the complexes decreases in the order K$^+$ > Rb$^+$. A similar trend was observed for the same compound by using solvent extraction in CDCl$_3$ [9]. The de-butylated 1,3-dimethoxy-calixcrown-5 (**2**) also shows selectivity for K$^+$ in methanol [14]. Table 1 also reveals that the stability constants are highest in 50 : 50 CHCl$_3$-MeOH for K$^+$, while the stability constants increase on increasing the percentage of CHCl$_3$ for Rb$^+$.

It was demonstrated that the complexation properties of calixcrowns depend on the size of the crown moiety and the conformation of the calix[4]crowns. The order of the complexation is cone < partial cone < 1,3 alternate [15]. To explain the stability in different solvents one may expect that an increasing amount of CHCl$_3$ in the solvent promotes conformational changes that cause the calixcrowns to adopt a 1,3 alternate conformation. Similar conformational changes were observed by Dijkstra et al. [14]. The ^{1}H NMR spectra that were recorded of the organic phase after extraction reveal the conformational changes of the calixcrowns upon complexation from the cone to a flattened partial cone conformation. However, calixcrown **1**, that is used here, has less conformational freedom than calixcrown **2**, which was used in the previous study. The solvent effect on the complexation of cyclic compounds with metal cations was also discussed in [16–18]. It was found that the stability of the complexes increases with decreasing power of the solvents as expressed by the donor numbers. Ashram [16] found that the stability constants for the complexes of alkali metal cations with ethyl *p*-*tert*-butylcalix[4]arenetetraethanoate in CH$_3$CN are higher than in CH$_3$OH. Tawarah et al. [17] also found that the stability constants of the inclusion complexes of alkali cations with 22-DD diaza crown ether, 211 and 221 cryptands in CH$_3$CN are higher than the

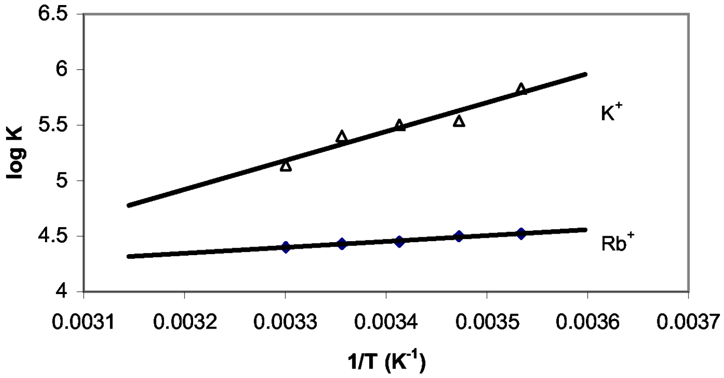


Fig. 3. Plot of log K vs. $1/T$ for the 1 : 1 binding of K^+ and Rb^+ with **1** in a (1 : 1) $CHCl_3$-methanol mixture.

published values for the same complexes in CH_3OH due to the difference in their donor numbers. Danil de Namor et al. [18] also found that the stability constants of sodium complexes with *p-tert*-butylcalix[4]arene ketone derivative in DMF/CH_3CN mixtures, increase as the percentage of CH_3CN increases in the solvent mixtures. The stability constants trend in different solvents that reveals from Table 1 agrees with the above discussion. The stability constants decrease as the percentage of CH_3OH in solution increases. This decrease is due to the greater desolvation energy of the cations in CH_3OH as compared to that in $CHCl_3$. The values of ΔH and ΔS were calculated from the least squares analysis of the log$K$ vs. $1/T$ plot which is shown in Figure 3. As shown in Table 1, it appears that the complexation of K^+ is enthalpy driven while the complexation of Rb^+ is more entropy driven. The complex with K^+ has shown the highest stability and reaction enthalpy. However, this complex formation is disfavoured by entropic contributions. The ring size effect may explain this result; the ionic size of K^+ fits nicely with the cavity size of the crown moiety of **1**. The X-ray structure of K^+ with 1,3-diethoxy-*p-tert*-butylcalix[4]arene crown-5 (**3**) was published [9]. In that structure the K^+ ion fitted nicely inside the crown moiety and is coordinated by seven oxygen atoms of the polyether ring and both ethoxy groups. The complex with Rb^+ has lower stability and less enthalpy than the complex with K^+, but it is favored by entropic contribution. This is probably due to the mismatch between the Rb^+ ionic size and the cavity size of the crown moiety of **1**. The ΔG values obtained in this study agree with what was published elsewhere, as shown in Table 1 [9].

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