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A Conductometric Study of Complexation Reaction Between Meso-octamethylcalix[4]pyrrole with Titanium Cation in Acetonitrile–Ethanol Binary Mixtures

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The equilibrium constants and thermodynamic parameters for complexation process between titanium (III) cation and meso-octamethylcalix[4]pyrrole were determined by conductivity measurements in acetonitrile–ethanol (AN–EtOH) binary mixture at different temperatures. The conductance data show that the stoichiometry of the (meso-octamethylcalix[4]pyrrole.[Ti(OH)-$(H_2O)_5$])$^{2+}$ complex in all binary mixed solvents is 1:1[I:M]. The stability of the formed complex is sensitive to the solvent composition and a non-linear behavior was observed for changes of log K_f of this complex versus the composition of the binary mixed solvents. The values of thermodynamic parameters (ΔH°_{c} and ΔS°_{c}) for formation of (meso-octamethylcalix[4]pyrrole.[Ti(OH)-$(H_2O)_5$])$^{2+}$ complex were obtained from temperature dependence of the stability constant using van't Hoff plots. The obtained results show that the formed complex is enthalpy destabilized, but entropy stabilized and a non-monotonic behavior was observed for variations of standard enthalpy and entropy changes versus the composition of the binary mixed solvents.

Keywords: meso-octamethylcalix[4]pyrrole, titanium (III) cation, Acetonitrile–ethanol binary solvents, Conductometry

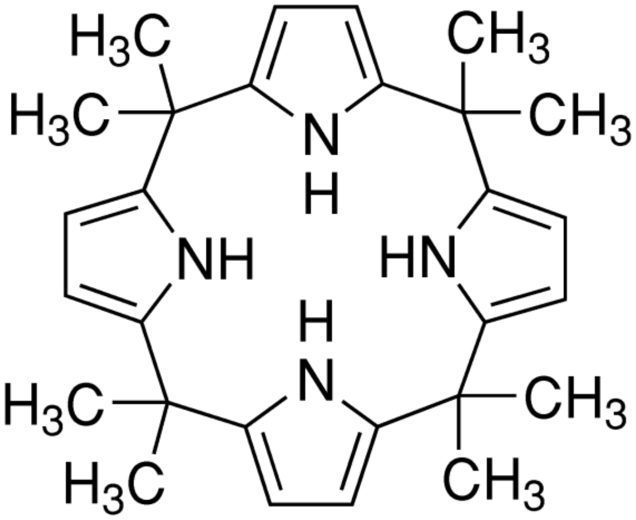
1. INTRODUCTION

Calixarenes have received extraordinary attention by many research groups as an important category of macrocyclic host molecules since last two decades. Calixarenes are versatile receptors with three dimensional structures which make them capable to form a stable complex with high selectivity and efficient binding properties towards the target ions [1-5]. Calixarenes with bowel-shaped cyclic structure can be synthesized through the ring-closing condensation of para-substituted phenols with formaldehyde which provide a hydrophobic cavity for encapsulation of a variety of cationic and anionic guest species, as well as neutral molecules and biological compounds [6, 7].

Calixarenes chemistry includes the study of non-covalent intermolecular interactions, which are mostly weak and reversible in nature. Calixarene construct complex with target ion through coordination bonds between the donor atoms such as oxygen, nitrogen or sulfur with the target cation, as well as π-coordination of the cation with the aromatic rings [8-12].

Different physicochemical techniques such as calorimetry [13], potentiometry [14, 15], spectrophotometry [16], conductometry [17-22] ,polarography [23-25] and NMR spectrometry [26, 27] have been used to study the complex formation between macrocyclic compounds with different metal ions in solutions. Among these various methods, the conductometric technique is a sensitive and inexpensive method with a simple experimental arrangement for such investigations. The study of various macrocyclic compounds in different solvents or solvent mixtures may indicate new approaches for developing pharmaceutical systems or a way to cross the blood organ barrier [28].

Numerous efforts has been done on the studies of macrocyclic compounds complexation with metal ions in pure organic solvents, yet comparatively less attention is put on the studies of complex formation in non-aqueous solvents [29-31]. Due to the widespread use of non-aqueous solvents in a wide range of pure and applied chemistry, which lead to quick development in chemical sciences technologies [32], it is worthwhile to extend our study to the mixed binary non-aqueous systems to see how the thermodynamics of the complexation are affected by the solvent composition.



Scheme 1. Chemical structure of meso-octamethylcalix[4]pyrrole

Titanium exists in aqueous solution as $Ti(H_2O)_6^{3+}$ (pH<1), $Ti(OH)(H_2O)_5^{2+}$ (1<pH<3), $Ti_2O(H_2O)_{10}^{4+}$ (pH=3), $Ti(OH)_{3+x}$ (3<pH) (x corresponding to the oxidation rate) and TiO_2 [33-35].

The dissolution and hydrolysis of titanium chloride (III) (which was employed as a source of titanium in current study) is a multivariate process.

The existence of each species depends on different variables such as pH, temperature, titanium concentration and hydrochloric acid concentration [35].

In order to investigate the influence of solvent properties on the interaction of metal ions with calixarenes, we report the results of thermodynamic study for complexation reaction between meso-octamethylcalix[4]pyrrole (Scheme 1) and titanium (III) cation in acetonitrile–ethanol (AN–EtOH) binary mixture at different temperatures using conductometric method in current study. It is noteworthy to mention that, there is no report on thermodynamic study of complex formation between meso-octamethylcalix[4]pyrrole with any metal cations.

2. EXPERIMENTAL PROCEDURE

2.1. Reagents and solvents

All reagents used in the current research are analytical reagent grade with the highest available purity which used without any further purification except for vacuum drying over P_2O_5. The novel ionophore namely meso-octamethylcalix[4]pyrrole and $TiCl_3$ were purchased from Fluka. The solvents: acetonitrile (AN) and ethanol (EtOH) with the highest purity from Merck were used as received.

2.2. Apparatus

The conductance measurements were performed using a digital Cyberscan conductivity/TDS/°C/°F meter model 510 CON in a thermostated water-bath with a constant temperature maintained within $\pm 0.01^{o}$C.

The electrolytic conductance was measured using a cell consisting of conductivity/TDS electrode comes with stainless steel rings to which an alternating potential was applied. A conductometric cell with a cell constant of 1.0 cm^{-1} and a built-in temperature sensor for automatic temperature compensation (ATC) was used throughout the studies.

2.3. Method

The experimental procedure to obtain the stability constant of (meso-octamethylcalix[4]pyrrole.$[Ti(OH)\text{-}(H_2O)_5])^{2+}$complex was as follow: a solution of metal salt (5.0×10^{-4} M) was placed in a titration cell and the conductance of the solution was measured, then a step-by-step increase in the calixarene concentration was performed by rapid transfer from calixarene solutions prepared in the same solvent (2.5×10^{-2}M) to the titration cell using a microburette. The conductance of the solution in the cell was measured after each addition at the desired temperature.

3. RESULTS

The conductometric profiles, for complexation of meso-octamethylcalix[4]pyrrole with titanium (III) cations in AN–EtOH binary mixture were studied at different temperatures. In these profiles the changes of molar conductivity (Λ_m) versus the ionophore (I) to metal cation (M) mole ratio ($[I]_t/[M]_t$) were studied at various temperatures. $[I]_t$ is the total concentration of the meso-octamethylcalix[4]pyrrole and $[M]_t$ is the total concentration of the titanium (III) cation. Four typical series of molar conductance values as a function of meso-octamethylcalix[4]pyrrole/$[Ti(OH)\text{-}(H_2O)_5]^{2+}$ cation mole ratio were plotted in pure EtOH, EtOH-AN (mol% EtOH=78.2), (mol% EtOH=37.4) and (mol% EtOH=4.5) binary systems as shown in Figure 1-4, respectively.

The stability constants for the formed complex at each temperature were calculated from the variation of molar conductance as a function of ionophore/metal cation mole ratios using non-linear least-squares GENPLOT computer program. The values of the stability constants (log K_f) for the (meso-octamethylcalix[4]pyrrole.$[Ti(OH)\text{-}(H_2O)_5])^{2+}$ complex in various solvent systems are listed in Table 1. The van't Hoff plots of Ln K_f versus 1/T for all of investigated systems were constructed as shown in Figure 5. The obtained results reveal that, in all cases, the van't Hoff plots are linear.

The changes in standard enthalpy (ΔH°_c) were obtained from the slope of the van’t Hoff plots by assuming that ΔC_p is equal to zero over the entire temperature range investigated and the changes in standard entropy (ΔS°_c) were calculated from the relationship $\Delta G^\circ_{c,298.15}=\Delta H^\circ_c - 298.15\Delta S^\circ_c$. The thermodynamic data are summarized in Table 2. The changes of log K_f of (meso-octamethylcalix[4]pyrrole.$[Ti(OH)\text{-}(H_2O)_5])^{2+}$ complex versus the mole fraction of ethanol in AN–EtOH binary system at different temperatures are shown in Figure 6.

4. DISCUSSION

As it can be seen from Figure 1-3, addition of meso-octamethylcalix[4]pyrrole to $[Ti(OH)(H_2O)_5]^{2+}$ cation in pure EtOH, EtOH-AN (mol% EtOH=78.2) and (mol% EtOH=37.4) binary solvent systems at different temperatures resulted in a decrease in molar conductivity by increasing the ionophore concentration, which indicates that the (meso-octamethylcalix[4]pyrrole.$[Ti(OH)\text{-}(H_2O)_5])^{2+}$ complex in the mentioned solutions is less mobile than free solvated $[Ti(OH)(H_2O)_5]^{2+}$ cation, but as it is obvious from Figure 4, addition of meso-octamethylcalix[4]pyrrole to $[Ti(OH)(H_2O)_5]^{2+}$ cation in EtOH-AN (mol% EtOH=4.5) binary solvent system at different temperatures resulted in an increase in molar conductivity by increasing the ionophore concentration, which indicates that the (meso-octamethylcalix[4]pyrrole.$[Ti(OH)\text{-}(H_2O)_5])^{2+}$ complex in EtOH-AN (mol% EtOH=4.5) binary solvent system is more mobile than free solvated $[Ti(OH)(H_2O)_5]^{2+}$ cation. The slope of the corresponding molar conductivity (Λ_m) versus ($[I]_t/[M]_t$) plots changes sharply at the point where the ionophore to cation mole ratio is about 1, which is an evidence for formation of a relatively stable 1:1 complex between ionophore and metal cation in these solvents.

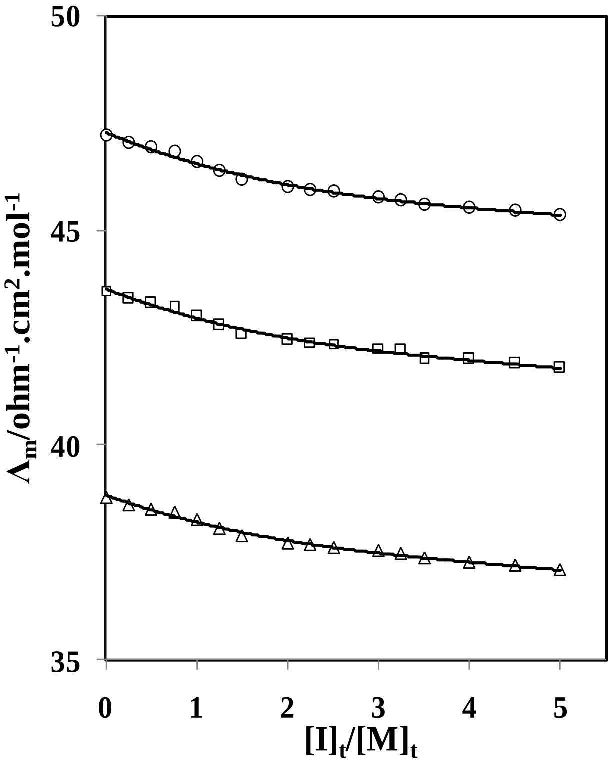


Figure 1. Molar conductance-mole ratio plots for (meso-octamethylcalix[4]pyrrole.[Ti(OH)-$(H_2O)_5$])$^{2+}$complexes in pure EtOH at different temperatures (Δ=25°C,□=35°C, ○=45).

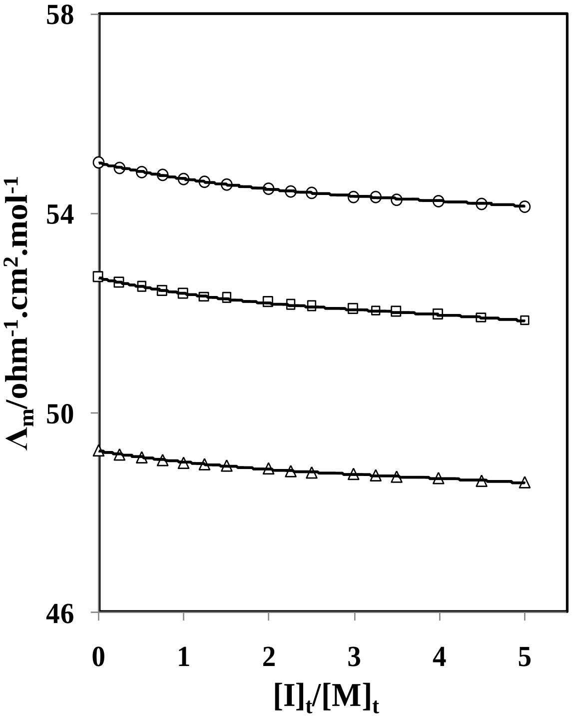


Figure 2. Molar conductance-mole ratio plots for (meso-octamethylcalix[4]pyrrole.[Ti(OH)-$(H_2O)_5$])$^{2+}$complexes in EtOH-AN binary system (mol% EtOH=78.2) at different temperatures (Δ= 25°C, □= 35°C, ○= 45°C).

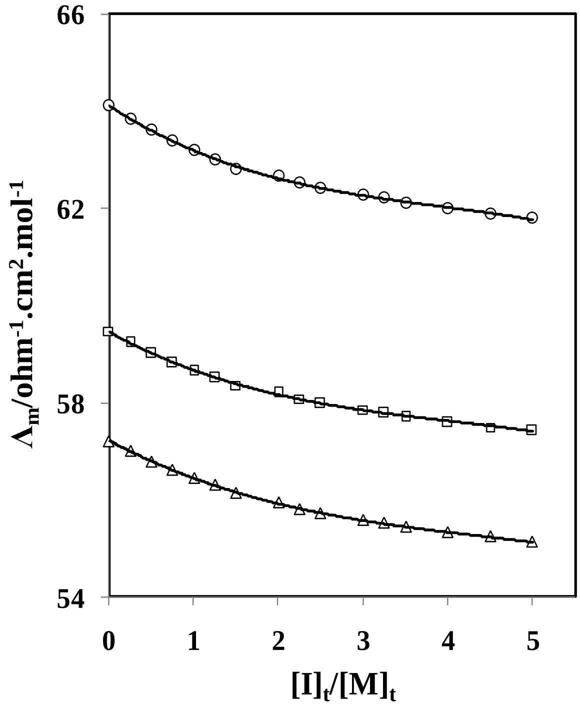


Figure 3. Molar conductance-mole ratio plots for (meso-octamethylcalix[4]pyrrole.[Ti(OH)-($H_2O)_5$])$^{2+}$complexes in EtOH-AN binary system (mol% EtOH=37.4) at different temperatures (Δ= 25°C, □= 35°C, ○= 45°C).

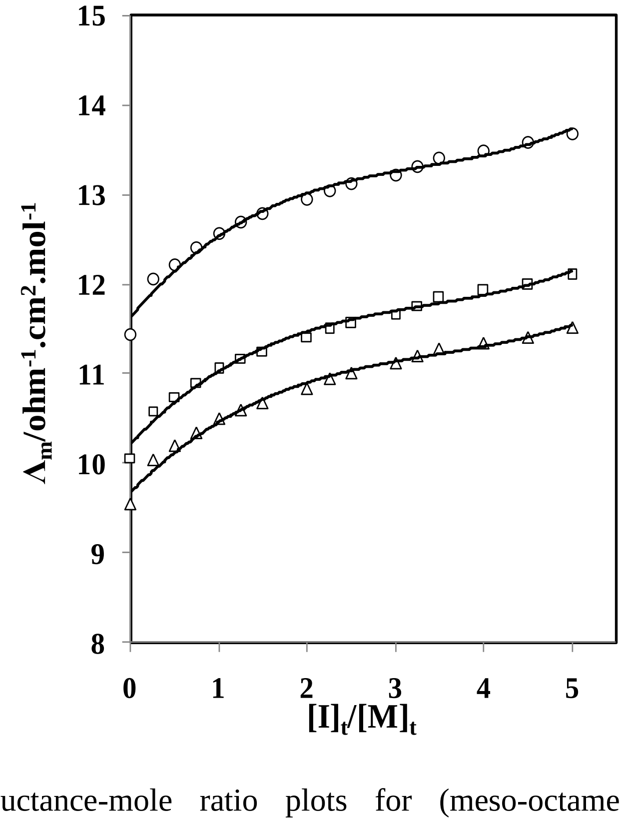


Figure 4. Molar conductance-mole ratio plots for (meso-octamethylcalix[4]pyrrole.[Ti(OH)-($H_2O)_5$])$^{2+}$complexes in EtOH-AN binary system (mol% EtOH=4.5) at different temperatures (Δ= 25°C, □= 35°C, ○= 45°C).

As it is demonstrated in Table 1, the stability constants increased by increasing the temperature which reveals that the complexation reaction between meso-octamethylcalix[4]pyrrole and $[Ti(OH)(H_2O)_5]^{2+}$ cation in these solvent systems is endothermic. The similar behavior for all formed complexes indicated that stronger complexes were formed at higher temperatures.

Table 1. *Log K_f* values of (meso-octamethylcalix[4]pyrrole.$[Ti(OH)\text{-}(H_2O)_5])^{2+}$ complex in EtOH-AN binary mixed solvent at different temperatures.

Complex	Log K_f ± SD[a]		
Solvent medium	25°C	35°C	45°C
(meso-octamethylcalix-[4]pyrrole.$[Ti(OH)(H_2O)_5])^{2+}$ EtOH-AN[b]			
4.5% EtOH - 95.5% AN	3.15 ± 0.09	3.18 ± 0.13	3.20 ± 0.11
18.3% EtOH - 81.7% AN	2.91 ± 0.04	2.97 ± 0.03	3.00 ± 0.03
37.4% EtOH - 62.6% AN	2.93 ± 0.02	2.99 ± 0.02	3.03 ± 0.03
57.3% EtOH - 42.7% AN	2.89 ± 0.09	2.93 ± 0.06	2.96 ± 0.06
78.2% EtOH - 21.8% AN	2.78 ± 0.05	2.86 ± 0.07	2.90 ± 0.03
Pure EtOH	2.87 ± 0.09	2.91 ± 0.09	2.95 ± 0.08

[a] *SD*=Standard deviation.

[b] Composition of binary mixture is expressed in mol% for solvent system.

Comparison of the stability constant values given in Table 1, reveals that for (meso-octamethylcalix[4]pyrrole.$[Ti(OH)\text{-}(H_2O)_5])^{2+}$ complex in binary solvents with higher concentration of EtOH with a relatively larger Gutmann donor number (DN: EtOH=19.0), $[Ti(OH)(H_2O)_5]^{2+}$ cations were strongly solvated and hardly can be complexed by the ionophore. However, the values of stability constant increase by increasing the concentration of AN with relatively smaller Gutmann donor number (DN: AN=14.1) in binary solvents, which is in accordance with the reverse order of their solvating ability as declared by Gutmann donor number.

It is known that the solvating ability of the solvent, as expressed by the Gutmann donor number, plays an important role in different complexation reactions [36]. Moreover, the stability and selectivity of the formed complexes are affected by some molecular factors such as the number and character of the donor atoms in the macrocyclic ring, the polarizability and charge density of the metal ion, the nature of substituents and cavity size of the macrocyclic compound, and the character of co-anion with the cationic species [31, 37-39].

As it is shown in Figure 6, the variation of the stability constant of (meso-octamethylcalix[4]pyrrole.$[Ti(OH)\text{-}(H_2O)_5])^{2+}$ complex versus the composition of AN–EtOH binary solvent system is not linear. This behavior is possibly related to the changes occurring in the structure of the solvent mixtures and therefore, changing in the solvation characteristics of the ionophore, cation and even the resulting complex in these binary solvent systems [40]. Moreover, there are some more parameters which may affect the complexation process, such as the preferential solvation of ionophore molecules and cations as well as the changes happened in their characteristics by changing the composition of solvents medium and temperature. Preferential solvation of ions by one of the components of a mixed solvent system depends on two factors: the relative donor–acceptor abilities of the component molecules towards the ion and the interactions between solvent molecules themselves. The solvating properties of the components in mixed solvents can even be significantly modified by solvent–solvent interactions when the energy of the latter is comparable with the energy difference of solvent–ion interactions for both components [41].

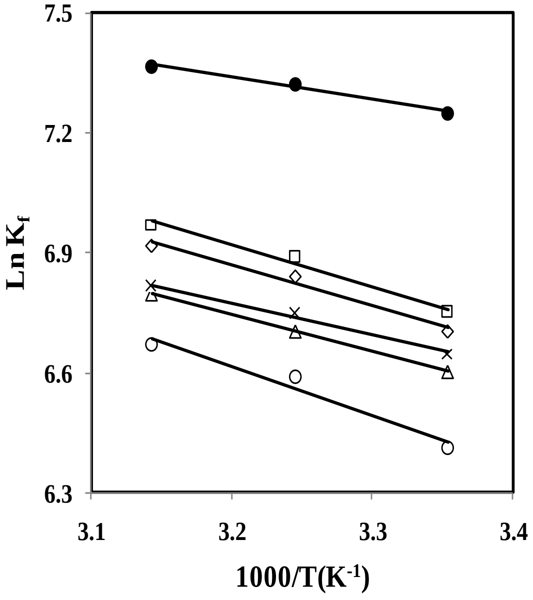


Figure 5. Van't Hoff plots for (meso-octamethylcalix[4]pyrrole.[Ti(OH)-(H_2O)$_5$])$^{2+}$ complexes in EtOH-AN binary systems (mol% EtOH: Δ=100, ○=78.2, ×= 57.3, □= 37.4, ◊=18.3, ●=4.5).

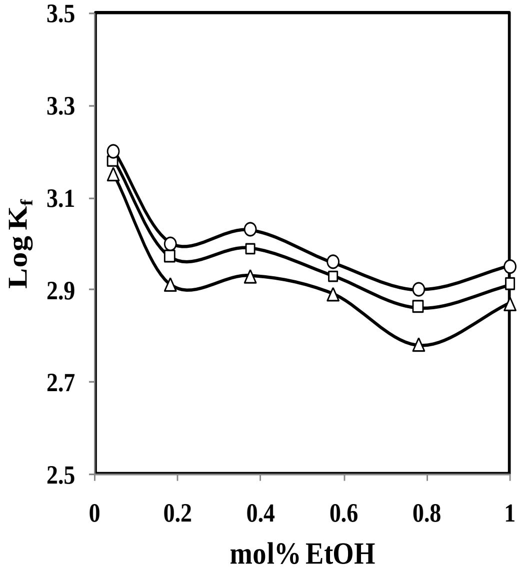


Figure 6. Changes of the stability constant (*log* K_f) of (meso-octamethylcalix[4]pyrrole.[Ti(OH)-(H_2O)$_5$])$^{2+}$ complexes with the composition of EtOH-AN binary systems at different temperatures (Δ= 25°C, □= 35°C, ○= 45°C).

Table 2 shows that, the thermodynamic data (ΔH°_{c}, ΔS°_{c}) for complexation reaction between meso-octamethylcalix[4]pyrrole and $[Ti(OH)(H_2O)_5]^{2+}$ cations vary significantly with the nature and composition of the mixed solvents as expected [36, 38, 42, 43]. This is due to variations in the extent of the contribution of such important parameters as solvation-desolvation of the species involved in the complexation reaction (i.e. $[Ti(OH)(H_2O)_5]^{2+}$ cation, ionophore and the resulting complex), and also the conformational changes of the macrocyclic ionophore upon complexation in the binary solutions. Even though many factors contribute to changes in enthalpy and entropy of complexation reactions, it seems that solvent properties such as donor number, dielectric constant and the isosolvation point can be used to explain the unusual changes of enthalpy and entropy as a function of solvent composition [44].

Table 2. Thermodynamic parameters for (meso-octamethylcalix[4]pyrrole.$[Ti(OH)\text{-}(H_2O)_5])^{2+}$ complex in EtOH-AN binary mixed solvent.

Complex Solvent medium	$\Delta G^{\circ}_{c} \pm SD^{a}$ **(kJ.mol^{-1})**	$\Delta H^{\circ}_{c} \pm SD^{a}$ **(kJ.mol^{-1})**	$\Delta S^{\circ}_{c} \pm SD^{a}$ **(J. mol^{-1} K^{-1})**
(meso-octamethylcalix-[4]pyrrole.$[Ti(OH)(H_2O)_5])^{2+}$ EtOH-AN^{b}			
4.5% EtOH - 95.5% AN	-17.97 ± 0.54	4.56 ± 0.58	75.57 ± 0.71
18.3% EtOH - 81.7% AN	-16.62 ± 0.21	8.38 ± 1.25	83.85 ± 4.13
37.4% EtOH - 62.6% AN	-16.73 ± 0.10	8.73 ± 1.02	85.39 ± 3.40
57.3% EtOH - 42.7% AN	-16.48 ± 0.50	6.56 ± 0.60	77.28 ± 1.11
78.2% EtOH - 21.8% AN	-15.90 ± 0.29	10.10 ± 1.93	87.20 ± 6.40
Pure EtOH	-16.37 ± 0.51	7.65 ± 0.02	80.56 ± 1.70

[a] *SD*=Standard deviation.

[b] Composition of binary mixture is expressed in mol% for solvent system.

The experimental values of standard enthalpy (ΔH°_{c}) and standard entropy (ΔS°_{c}) show that, the thermodynamic parameters for complexation reaction between meso-octamethylcalix[4]pyrrole and $[Ti(OH)(H_2O)_5]^{2+}$ cations in these solutions, did not vary monotonically with the solvent composition. A non-monotonic behavior has also been observed for thermodynamic functions of several macrocyclic compound-metal ion complex formation in some binary mixed solvents [17, 19, 29, 39, 40]. The observed behavior has been discussed in terms of preferential solvation of the calixarene molecules which in turn depends quantitatively on the structural and energetic properties of the mixed solvent system. Since there are many factors, which contribute to changes of enthalpy and entropy of complexation reactions, therefore, we should not expect a monotonic relationship between these thermodynamic quantities and the solvent composition of these mixed solvents [28].

As it is obvious from Table 2, the changes in ΔH°_{c} for the complexation process in the most cases are negligible whereas the changes in ΔS°_{c} are significant. Hence, this thermodynamic quantity is the main driving force for the formation of (meso-octamethylcalix[4]pyrrole.$[Ti(OH)\text{-}(H_2O)_5])^{2+}$ complex in EtOH-AN binary solvent solutions. The changes of solvation, steric deformation of the ionophore and intermolecular ionophore-ionophore repulsions resulted in the change of ionophore enthalpy in complexation process. The increase in degree of freedom which caused by desolvation of cation might result in some positive entropic gain, as well as releasing the solvent molecules that involved in the interaction with ionophore. Moreover, the solvent-solvent interactions and changing in flexibility of ionophore upon complexation contributed to changes in entropy [28]. The enthalpy and entropy values of complexation reaction are influenced by the amount of cation-solvent, macrocyclic compounds-solvent, complex-solvent and even solvent-solvent interactions [20, 22].

4. CONCLUSIONS

The solvent nature plays a critical role in stabilizing the host-guest complexation process. The solvation capacities of ionophore and metal cations, thermodynamic stability, stoichiometry, selectivity and exchange kinetics of cation-ionophore complexes vary with the alteration of the binary solvent composition. The stoichiometry of the (meso-octamethylcalix[4]pyrrole.$[Ti(OH)\text{-}(H_2O)_5])^{2+}$ complex in all composition of EtOH-AN binary mixed solvents is 1:1[I:M].

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