

A CONDUCTOMETRIC STUDY ON THE EFFECT OF SOLVENT UPON COMPLEX FORMATION BETWEEN KRYPTOFIX22DD WITH Ho^{3+} METAL CATION IN ORGANIC SOLVENTS

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ABSTRACT. The complexation reaction between Ho^{3+} cation with macrocyclic ligand kryptofix22DD was studied in ethyl acetate (EtOAc), methanol (MeOH), propylene carbonate (PC), tetrahydrofuran (THF) at different temperatures by conductometric method. Kryptofix22DD forms a 1:1 complex with Ho^{3+} cation. The stability of $(\text{kryptofix22DD.Ho})^{3+}$ complex changes with the type of the organic solvents and also with temperature. The stability constant of the complex in the non-aqueous solvents varies in order: $\text{EtOAc} \geq \text{THF} > \text{PC} \geq \text{MeOH}$. By plotting the van't Hoff diagrams, the values of standard thermodynamic parameters such as enthalpy (ΔH°), entropy (ΔS°) and Gibbs free energy (ΔG°), for formation of $(\text{kryptofix22DD.Ho})^{3+}$ complex were obtained. The results showed that the entropy and enthalpy of complexation reaction between kryptofix22DD with Ho^{3+} metal cation depend on the nature of the solvents.

KEY WORDS: Kryptofix22DD, Ho^{3+} cation, Organic solvents, Complexation, Conductometry

INTRODUCTION

Crown ethers as an important category of macrocyclic host molecules are a branch of macrocyclic compounds that are efficiently applicable in various fields and therefore, have received extraordinary attention by many researchers [1-4]. These hosts have three dimensional structures and therefore, can form stable complex with various cations. The interactions between host and guest are via oxygen, nitrogen or sulfur heteroatoms in the skeleton of crown ether with cations [5-11]. Moreover, due to different hole size, they can form various types of complexes with high selectivity. Also, the interaction between crown ether and target ion is non-covalent. Therefore, one of the important aspects is that the complexation process is reversible and they can be used as phase transport catalyst [12-13].

Holmium is a rare-earth element and part of lanthanide series. It has the highest magnetic permeability of any element and therefore is used for the pole pieces of the strongest static magnets. Because holmium strongly absorbs neutrons, it is also used as a burnable poison in nuclear reactors. Lanthanide complexes are of interest due to their importance in optical imaging of cells, as luminescent chemosensors for medical diagnostics, contrast reagents for medical magnetic resonance imaging, shift reagents for NMR spectrometry, as well as, their potential applications in imaging applications [14-16].

Some techniques such as, potentiometry [17, 18], conductometry [19-23], spectrophotometry [24], polarography [25-26], calorimetry [27] and NMR spectrometry [28-29] 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 may indicate new approaches for developing pharmaceutical systems.

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Solvent has a critical role in complex formation. Investigations on the stability of complexes in various solvents lead to developing pharmaceutical systems [30]. Use of non-aqueous solvents in a wide range of pure and applied chemistry leads to quick development in chemical sciences technologies [31]. Also the complex formation between cations and macrocyclic guests depends on temperature. Also thermodynamic has a significant effect on the stability of complex. Therefore, thermodynamic parameters are of interest for scientific solvent selection in various applications [5-9]. Since little attention has been paid to rare earth complexation, hence, information about the coordination behavior of crown ethers towards these metal cations is relatively scarce. To study the effect of solvent on the interaction between cation and ligand, some of organic solvents were selected and investigated. It is noteworthy to mention that, there is no report on thermodynamic study of complex formation between macromolecules such as kryptofix-22DD and Ho^{3+} cation.

In this work the complexation process between kryptofix22DD and Ho^{3+} cation in ethylacetate (EtOAC), methanol (MeOH), propylene carbonate (PC), tetrahydrofuran (THF) at different temperatures using the conductometric method was studied.

EXPERIMENTAL

Materials and methods

Kryptofix22DD (Merck) and holmium nitrate ($\text{Ho}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) (Riedel) were used without further purification. The solvents: ethylacetate (EtOAC), methanol (MeOH), propylene carbonate (PC), tetrahydrofuran (THF), all from (Merck), were used with the highest purity.

The experimental procedure to obtain the formation constant of the complex was as follows: a solution of metal salt (1×10^{-4} M) was placed in a titration cell and the conductance of the solution was measured, then a step-by-step increase in the crown ether concentration was performed by a rapid transfer from crown ether solution in the same solvent (2×10^{-3} M) to the titration cell, using a microburette and the conductance of the resulted solution was measured after each step at the desired temperature. The conductance measurements were performed on digital Metrohm conductivity apparatus (model 712) in a water bath Julabo (model F12) thermostated with a constant temperature maintained within ± 0.01 °C. The electrolytic conductance was measured using a cell consisting of two platinum electrodes to which an alternating potential was applied. A conductometric cell with a cell constant of 0.84 cm^{-1} was used throughout the studies.

Data analysis program

The 1:1 complexation of a metal cation, M^{n+} , with a crown ether (L) is represented by the following equilibrium:



The corresponding equilibrium constant, K_p , is given by:

$$K_f = \frac{[\text{ML}^{n+}] f_{\text{ML}^{n+}}}{[\text{M}^{n+}] f_{\text{M}^{n+}} \cdot [\text{L}] f_L} \quad (2)$$

where $[\text{ML}^{n+}]$, $[\text{M}^{n+}]$, $[\text{L}]$ and f represent the equilibrium molar concentration of the complex, free cation, free ligand and the activity coefficient of the species indicated, respectively.

Under the highly dilute condition which we used, in this investigation, the activity coefficient of the uncharged ligand, f_L , can be reasonably assumed as unity [12, 13]. With using

of the Debye-Huckel limiting law [14], we can neglect from the f_M^{n+} , f_{ML}^{n+} values in equation 2. Thus the complex formation constant in term of the molar conductance can be expressed as:

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} = \frac{\Lambda_M \cdot \Lambda_{obs}}{\Lambda_{obs} - \Lambda_{ML}} \quad (3)$$

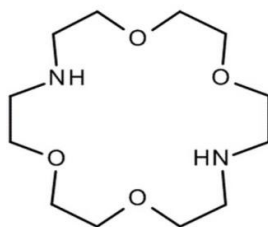
where

$$C_L = C_M (\Lambda_M \cdot \Lambda_{obs}) / (\Lambda_M \cdot \Lambda_{ML}) \quad (4)$$

Here Λ_M is the molar conductance of the metal ion before addition of the ligand, Λ_{ML} is the molar conductance of the complexed ion, Λ_{obs} is the molar conductance of the solution during titration, C_L is the analytical concentration of the L added, and C_M is the analytical concentration of the metal ion. The complex formation constant, K_f , and the molar conductance of complex, Λ_{ML} , were obtained by computer fitting of equations 3 and 4 to molar conductance as a function of ligand/metal cation mole ratio data, using a non-linear least-squares program GENPLOT [32]. All calculated stability constants are summarized in Table 1. The details of calculation of the stability constants of metal ion complexes by the conductometric method have been described elsewhere [33].

RESULTS AND DISCUSSION

The structure of kryptofix22DD is shown in Scheme 1.



Scheme 1. Structure of kryptofix22DD.

The complex formation between kryptofix22DD and Ho^{3+} cation in ethylacetate (EtOAc), methanol (MeOH), propylene carbonate (PC), tetrahydrofuran (THF) was investigated by molar conductance changes upon addition of the ligand to Ho^{3+} cation solution at 15, 25, 35 and 45 °C. Some of the resulting molar conductance (Λ_m) vs. macrocycle to Ho^{3+} molar ratio ($[L]_t/[M]_t$) plots are shown in Figs.1 and 2. As is evident from these Figures, addition of Kryptofix22DD to a solution of Ho^{3+} cation in pure PC and MeOH at different temperatures results in an increase in molar conductivity with an increase in the ligand concentration which indicates that the $(kryptofix22DD.Ho)^{3+}$ complex is more mobile than free solvated Ho^{3+} cation. Similar behaviour was observed in other solvents. The slope of the corresponding molar conductivity versus ligand/cation mole ratio plots changes at the point where the ligand to cation mole ratio is about 1, which is an evidence for formation of a relatively stable 1:1 complex.

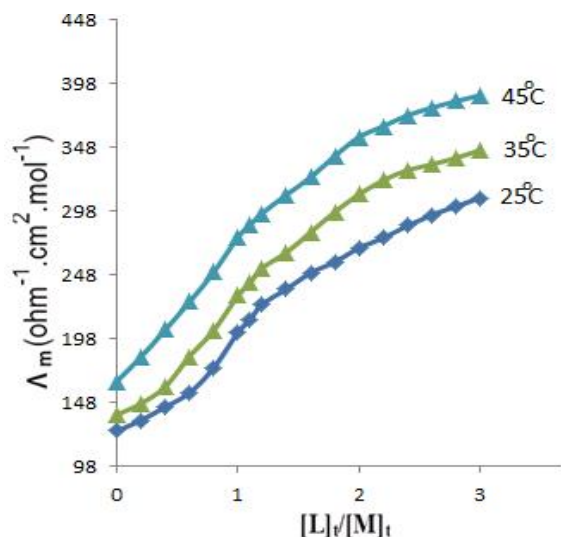


Figure 1. The changes of conductance versus the ligand to cation ratio in different temperatures in PC solvent.

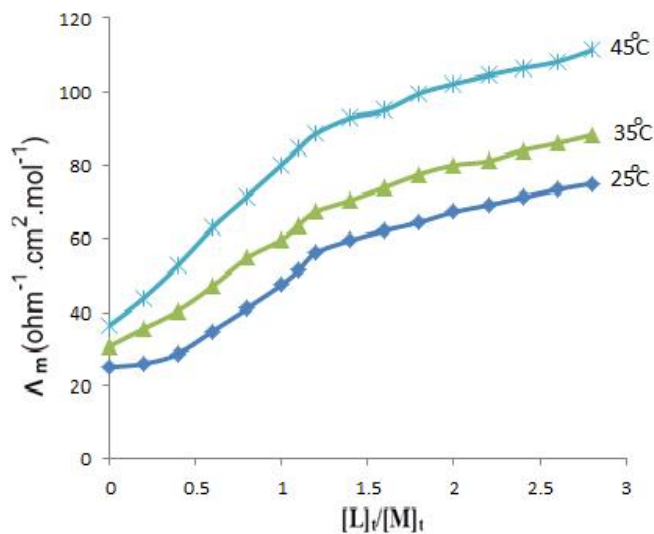


Figure 2. The changes of conductance versus the ligand to cation ratio in different temperatures in MeOH solvent.

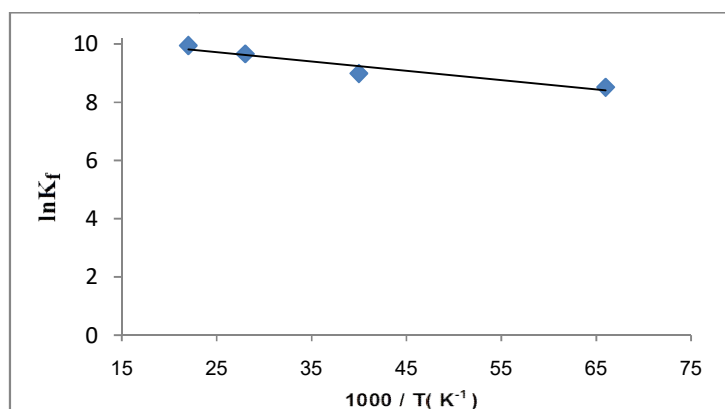
The $\log K_f$ data in Table 1 show that the stability constant of $(\text{kryptofix22DD.Ho})^{3+}$ complex is higher in PC and MeOH ($DN = 19$). The solvation of the ligand and the metal cation is influenced by the donor ability and dielectric constant of the solvent. It is known that the donor ability and dielectric constant of the solvent play an important role in complexation reactions [34-35].

Table 1. Log K_f values of (kryptofix22DD.Ho)³⁺ complexes in organic solvents at different temperatures.

Medium ^b	Log $K_f \pm SD^a$			
	15 °C	25 °C	35 °C	45 °C
PC	3.69±0.1	3.90±0.06	4.19±0.08	4.32±0.19
MeOH	3.49±0.16	3.61±0.10	3.79±0.07	2.93±0.24
EtOAc	4.40±0.25	c	c	c
THF	4.27±0.06	3.89±0.13	d	c

^aSD= standard deviation. ^bThe concentration of metal cation was 1.0×10^{-4} M. ^cThe data are not fitted to equation. ^dWith high uncertainty.

The stability constant of (kryptofix22DD.Ho)³⁺ complex in various solvent at 25 °C varies in order: EtOAc ($\epsilon = 6.02$) \geq THF ($\epsilon = 7.58$) > PC ($\epsilon = 64.1$) \geq MeOH ($\epsilon = 32.7$). Various properties of solvent may affect the formation constant of the complex. The dielectric constant of EtOAc and THF are low, therefore the interaction between ligand and cation is more appropriate than other solvents. Comparison between PC and MeOH shows, the complex in PC is a little more stable than MeOH. This phenomenon may be due to lower donor number of PC (DN = 15.1) in comparison to MeOH (DN = 19). In MeOH, the solvent molecules solvate the cations and compete with the kryptofix22DD for Ho³⁺ cations.

Figure 3. van't Hoff plot for (kryptofix22DD.Ho)³⁺ complex formation in PC solvent.

Assuming that the activity coefficients of the cation and the complex have the same values, K_f is a thermodynamic equilibrium constant on the molar concentration scale, related to the Gibbs standard free energy of complexation reaction, ΔG_c° . The van't Hoff plots of $\ln K_f$ versus $1/T$ in all cases were linear. The changes in the standard enthalpy (ΔH_c°) for complexation of the kryptofix22DD with Ho³⁺ cation were obtained from the slope of the van't Hoff plots. The changes in standard entropy (ΔS_c°) were calculated from the relationship ($\Delta G_c^\circ, 298.15 = \Delta H_c^\circ - 298.15\Delta S_c^\circ$). The plots for PC and MeOH are shown in Figures 3 and 4. For example, as is shown in Figure 3 the slope of the plot for PC is negative; therefore, the ΔH_c° value is positive which is an evidence for an endothermic reaction between kryptofix with Ho³⁺ cation in this solvent system.

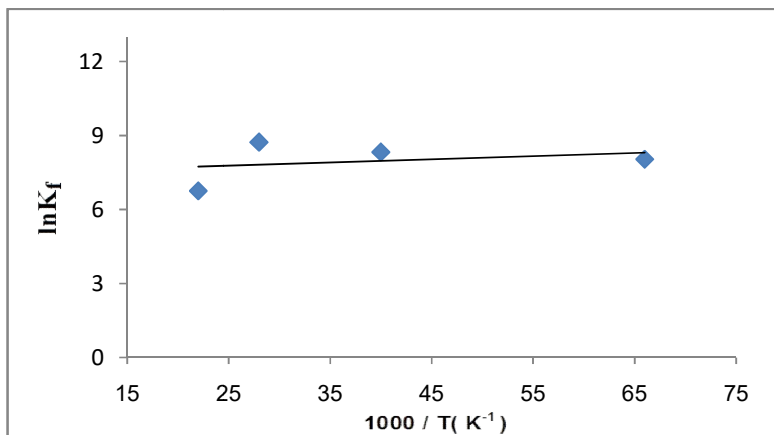


Figure 4. van't Hoff plot for (kryptofix22DD.Ho)³⁺ complex formation in MeOH solvent.

The experimental values of standard enthalpy (ΔH°_c) and standard entropy (ΔS°_c) which are given in Table 2, show that in the case of MeOH, the complex is enthalpy and entropy stabilized, but in PC the enthalpy is not appropriate and only entropy of the complexation reaction is the principal driving force for formation of (kryptofix22DD.Ho)³⁺ complex in solutions.

Table 2. Thermodynamic parameters for (kryptofix22DD.Ho)³⁺ complex in organic solvents.

Medium	$\Delta G^\circ_c \pm SD^a$ (25°C) (kJ/mol)	$\Delta H^\circ_c \pm SD^a$ (kJ/mol)	$\Delta S^\circ_c \pm SD^a$ (J/mol K)
PC	-22.4±0.4	73.1±0.01	320±3
MeOH	-20.6±0.7	-16.5±0.01	13.9±6

^aSD = standard deviation. ^bThe concentration of each metal cation was 1.0×10^{-4} M.

As expected, the values of ΔH°_c and ΔS°_c depend strongly on the nature of the solvents. The value and the sign of the standard entropy changes are expected to vary with different parameters, such as changes in flexibility of the macrocyclic ligand during the complexation process and the extent of cation-solvent, ligand-solvent and also the complex-solvent interactions.

CONCLUSION

In this work, the complex formation of Ho³⁺ cation with kryptofix22DD was investigated and the effect of type of organic solvent (ethylacetate (EtOAc), methanol (MeOH), propylene carbonate (PC), tetrahydrofuran (THF)) and also effect of temperature on the complex formation was studied by conductometric method. The ratio of ligand to cation was 1:1. The stability constant of the complex varies in order: EtOAc ≥ THF > PC ≥ MeOH. Moreover some thermodynamic parameters for formation of (kryptofix22DD.Ho)³⁺ complex in different solvents were obtained.

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