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Effect of magnetic field on property of a non-aqueous solvent upon complex formation between kryptofix 22DD with yttrium (III) cation

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Abstract To understand the effect of a magnetized solvent upon complexation processes between the metal ions and the ligands, we studied the complexation reaction between Y^{+3} cation with the kryptofix 22DD, in non-magnetized and magnetized methanol solvents at different temperatures using the conductometric method. Addition of kryptofix 22DD to the cation solution causes a continuous increase in the molar conductivities which indicates that the mobility of the complexed cation is higher than the uncomplexed one in both non-magnetized and magnetized methanol solvents. The conductance data show that the stoichiometry of the complex formed between the ligand and Y^{3+} cation is 1:1(M:L). The value of stability constant of (kryptofix 22DD.Y)$^{3+}$ complex was determined from conductometric data using a non-linear least-square program (GENPLOT). The results obtained in this investigation, show that the stability constant of the complex decreases when we use magnetized methanol solvent.

Introduction

Cryptands and their derivatives due to their ability to bind strongly and selectivity to various metal cations and substrate molecules can find use in many diverse processes such as construction of electrodes [1–3] and stationary phase in chromatography columns [4, 5]. Some kryptofixes are used to produce 18F-Pharmaceuticals [6] and to extract metal ions [7].

The effects of magnetic fields on water were discovered in the early 1900s by Danish Physicist Hendrick Antoon Lorenz. He received the Nobel Prize in 1902 for his discovery of the effects of magnetic fields on water [8]. This technique consists of exposing water to a magnetic field. Experiments show that a lot of properties of magnetized water such as dielectric constant [9], viscosity [10, 11] and surface tension [12] are changed as compared with that of non-magnetized water. Magnetized water has extensive applications in industry, agriculture and medicine, for instance, it is helpful to aid digestion of food [13], eliminate dirt in industrial boilers [14, 15], reduce the corrosion rate of steel [16] and remove heavy metals in chemical industry [17].

In the host–guest recognition processes, the solvent plays a critical role in local structure optimization and complex stabilization. Thus, the complex stability is known to vary sometimes drastically according to the chemical and physical properties of the solvent in which the reactions occur [18]. This suggests the need for more detailed understanding of non-covalent interactions between the metal ions, natural molecules and solvent, and also for accurate evaluation of the critical parameters on these interactions.

One approach to achieve a detailed understanding of these interactions is to study the influence of magnetic field on physicochemical properties of solvents and consequently upon formation of metal ion–macrocyclic ligand complexes in solutions. Investigation of the effect of a magnetic field on complexation of crown compounds with

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metal ions is of interest, because crown compounds are models for antibiotics and some other drug treatments in biological systems [19]. Golizadeh and Eshaghi [20] have investigated the effect of magnetic field on complexation of an 18-crown-6 with potassium ion in aqueous media, but to the best of our knowledge the data about the stability constants of metal ion complexes with macrocyclic ligands in non-aqueous magnetized solvents have not been yet investigated.

It is the intend of this work to offer a tangible scientific concept about the effect of magnetized solvent upon complexation of kryptofix 22DD with yttrium (III) cation and to investigate, whether the magnetized solvent can change the stability constant of the complex formed between the kryptofix 22DD and yttrium (III) cation.

Experimental

Reagents and solvent

Y $(NO_3)_3 \cdot 6H_2O$, kryptofix 22DD (4,13-didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane) with the highest purity were purchased from Merck (>99 % purity) and were used without any further purification. Methanol (from Merck, >99 % purity) was used without further purification. The conductivity of methanol solvent was <3.0×10^{-7} S^{-1} cm^{-1} at 298.15 K. The experimental procedure to obtain the stability 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 of the kryptofix 22DD solution prepared in the same solvent (2×10^{-3} M) was carried out by a rapid transfer to the titration cell using a microburette and the conductance of the solution in the cell was measured after each transfer at the desired temperature. This procedure is exactly carried out for the magnetized methanol solvent. The magnetized solvent is immediately used after passing through the magnetic field for 2 min.

Apparatus

The conductance measurements were performed on a digital Jenway conductivity apparatus (Model 4510), in a water bath thermostated at a constant temperature which maintained within ±0.1 °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 0.98 cm^{-1} was used throughout the studies.

The static magnetic field in a compact form, a unit called "AQUA CORRECT" was used. The equipment has a coaxial static magnetic system of 6000G field strength which was imported from Germany (H.P.S Co.) (DN = 20, 3/4 in., flow 2 m^3/h) for the experiments.

The equipment was connected from one end to the liquid pump and the other end to the pipelines of solvent reservoir. The solvent had to flow through a coaxial static magnetic gap, and came back to the solvent reservoir. Therefore, the solvent could pass through the magnetic field for many times, in a closed cycle.

Results and discussion

The changes of molar conductivity (Λ_m) versus the ligand to metal cation mole ratio, ($[L]_t/[M]_t$), for complexation of kryptofix 22DD with Y^{3+} cation were studied in both non-magnetized and magnetized methanol solvents at different temperatures. Figures 1 and 2 show the differences between the molar conductivity of the non-magnetized and magnetized methanol solvents, respectively. As is clearly seen in Figs. 1 and 2, in all cases, addition of the macrocyclic ligand to Y^{3+} cation solution causes a continuous increase in the molar conductance at different temperatures. This result may be explained on the basis of the solvation sphere [21]. It seems that the Y^{3+} cation is solvated to a high extent in these organic solvent. Upon complexation of the metal cation with kryptofix 22DD in these organic solvent, the
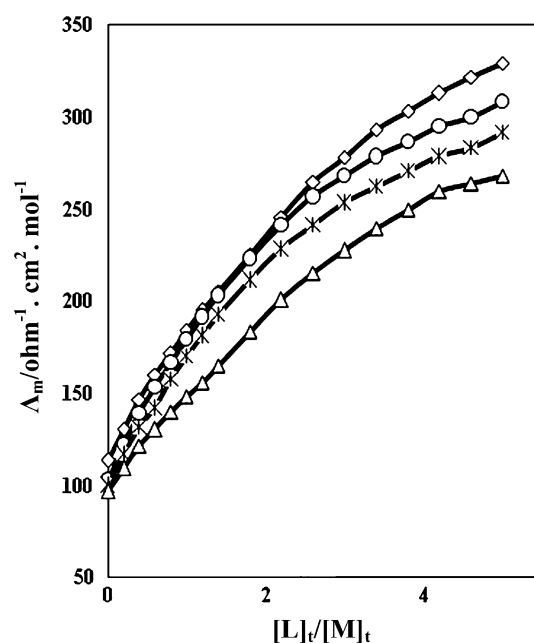

Fig. 1 Molar conductance–mole ratio plots for (kryptofix 22DD.Y)$^{3+}$ complex in non-magnetized methanol solvent at different temperatures: 15 °C (*open diamond*), 25 °C (*open circle*), 35 °C (*asterisk*), 45 °C (*open triangle*)

Fig. 2 Molar conductance–mole ratio plots for (kryptofix 22DD.Y)$^{3+}$ complex in magnetized methanol solvent at different temperatures: 15 °C (*open diamond*), 25 °C (*open circle*), 35 °C (*asterisk*), 45 °C (*open triangle*). Exposed time: 2 min
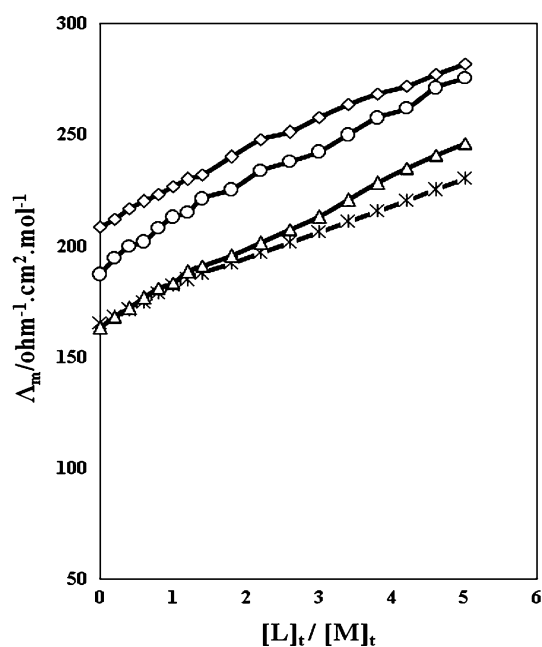

Fig. 3 The experimental data and fitting curve for (kryptofix 22DD.Y)$^{3+}$ complex in non-magnetized methanol solvent at 25 °C

cryptand molecule replaces the solvation sheath around the metal ion, and as a result, the moving complex becomes less bulky and, therefore, more mobile than the free solvated Y^{3+} cation in solution.

From Figures 1 and 2, it can be seen that the slope of the corresponding molar conductivity versus the ligand/cation mole ratio plots changes at the point where the ligand to cation mole ratio is about one, which is an evidence for the formation of a relatively stable 1:1[M:L] complex in non-magnetized and magnetized methanol solvents. The 1:1 binding of a metal cation with the ligand can be expressed by Eq. (1) and the corresponding equilibrium constant, K_f, is given by Eq. (2):

$$M^{n+} + L \leftrightarrow ML^{n+} \tag{1}$$

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} \times \frac{f_{ML^{n+}}}{f_{M^{n+}} + f_L} \tag{2}$$

where [ML^{n+}], [M^{n+}], [L] and f, represent the equilibrium molar concentrations of the complex, cation, ligand and the activity coefficient of the species indicated, respectively. Under the highly diluted experimental conditions which we used in this study, the activity coefficient of the uncharged ligand f_L, can be reasonably assumed as unity [22]. Using Debye–Huckel limiting law leads to the conclusion that, $f_{M^{n+}} \sim f_{ML^{n+}}$, therefore, the activity coefficients in Eq. (2) could be canceled. Consequently, the complex formation constant in terms of the molar conductance can be expressed by Eq. (3); [22, 23]:
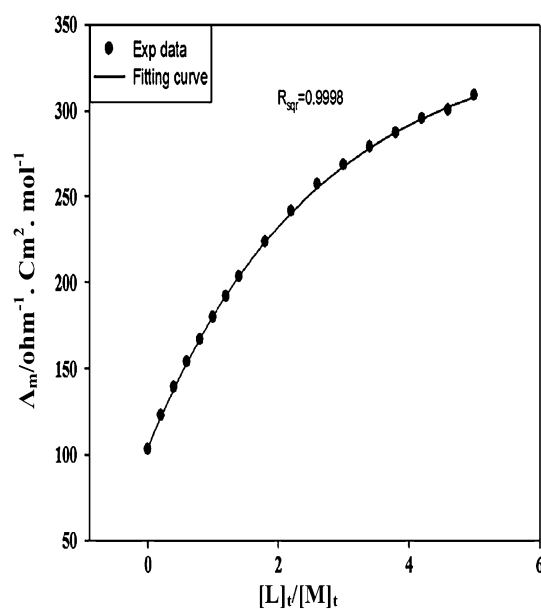
$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]}. \tag{3}$$

Where

$$[L] = C_L - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_M - \Lambda_{ML})}. \tag{4}$$

Here, Λ_M is the molar conductance of the metal nitrate before addition of the ligand, Λ_{obs} is the molar conductance of solution during titration and Λ_{ML} is the molar conductance of the complexed ion. C_L is the analytical concentration of the ligand added and C_M is the analytical concentration of the metal nitrate. The complex stability constant, K_f, was obtained by computer fitting of Eqs. (3) and (4) to the molar conductance–mole ratio data using a non-linear least-squares program GENPLOT [24].

To make the 1:1 [M:L] complexation model more clear, the fitting and experimental curves for (kryptofix 22DD.Y)$^{3+}$ complex in non-magnetized and magnetized methanol solvents are shown in Figs. 3, 4, respectively. As is evident from these figures, there is a very good agreement between the fitting and the experimental data.

Also, to obtain further information about the conformational change of kryptofix 22DD upon complexation to the yttrium (III) cation, the molecular structures of the uncomplexed ligand and its 1:1 yttrium (III) complex were computed with quantum calculations. All calculations were carried out with the GAUSSIAN 09 software package [25], applying the modern density functional theory, DFT method. The structure of free ligand was optimized using the Lanl2dz basis set at the B3LYP level of theory. The optimized structure of the ligand was then used to find out
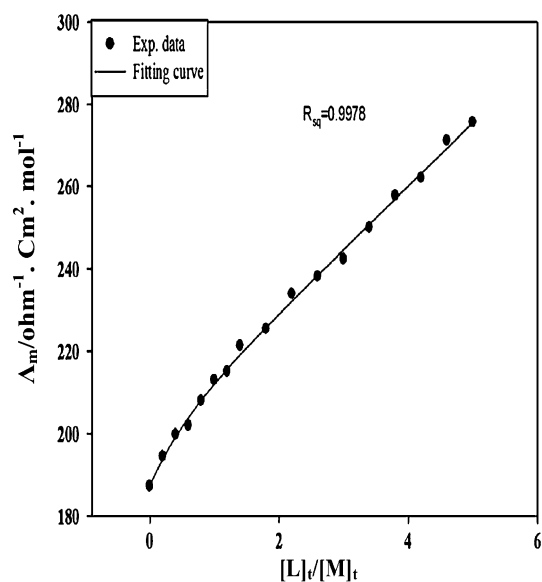
Fig. 4 The experimental data and fitting curve for (kryptofix 22DD.Y)$^{3+}$ complex in magnetized methanol solvent at 25 °C

the initial structure of its 1:1 yttrium (III) complex. Finally, the structure of the resulting 1:1 complex was optimized using the Lanl2dz basis set at the B3LYP level of theory. All calculations were carried out in the gas phase. The top and side views of optimized structures of kryptofix 22DD and (kryptofix 22DD.Y)$^{3+}$complex are shown in Fig. 5.

As it is obvious from Fig. 5a, b, the ligand forms a more or less planar. But interestingly, in the optimized structure of the 1:1 (kryptofix 22DD.Y)$^{3+}$complex (Fig. 5c, d), the yttrium (III) ion is well incorporated inside the twisted macrocyclic ligand and coordinated to six donating atoms of the ligand, including four oxygen and two nitrogen atoms. It is interesting to note that when the metal ion is added to the ligand, the ligand twisted and completely deformed from its planar shape. Moreover, the orientation of two carbon chains which are attached to the ring is changed when compared to the free ligand.

More interesting is the fact that the slope of the molar conductivity curves in the case of magnetized methanol solvent is less compared to that of the non-magnetized
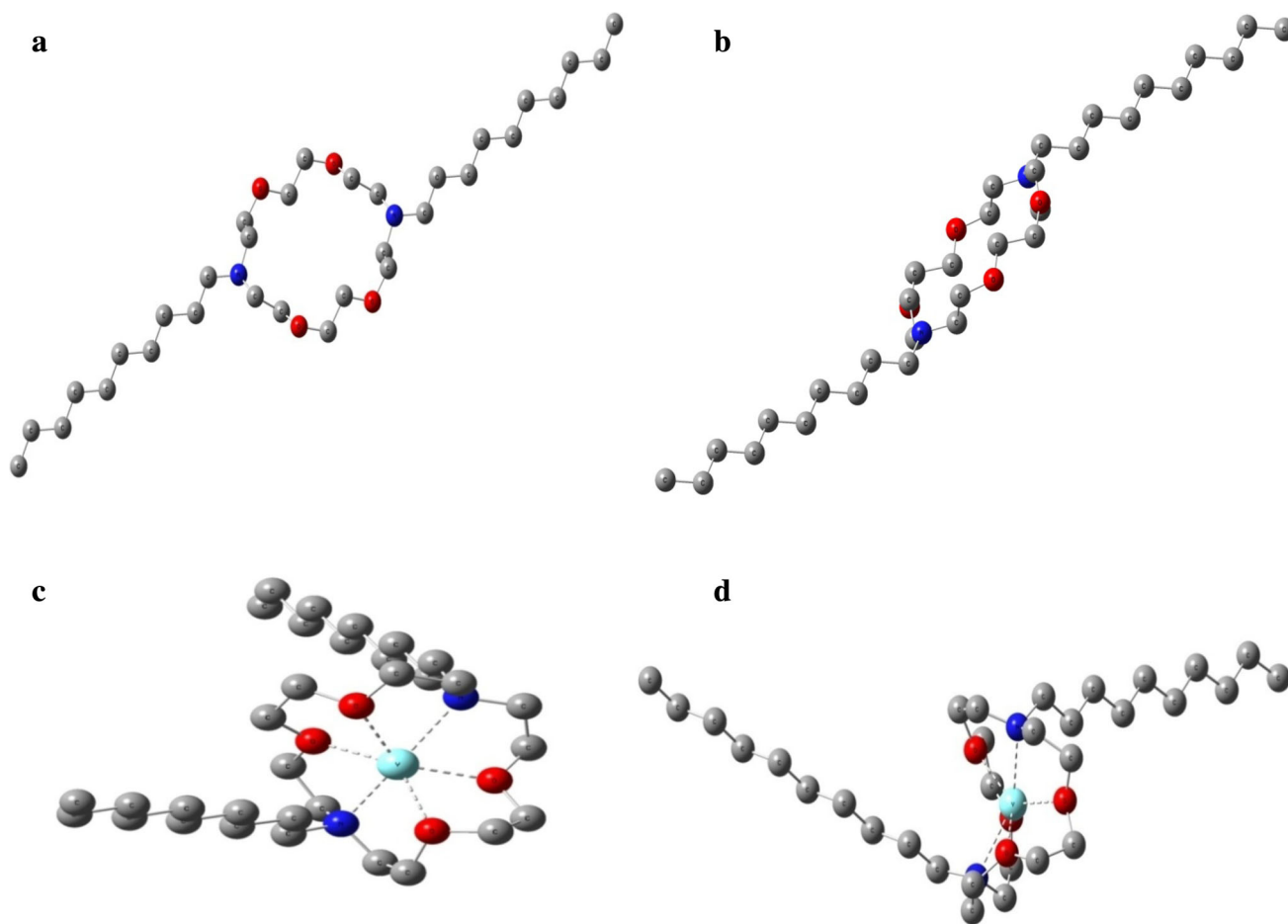

Fig. 5 Optimized structures of the kryptofix 22DD: **a** Top view, **b** side view and (kryptofix 22DD.Y)$^{3+}$ complex: **c** Top view, **d** side view

methanol solvent (Figs. 1, 2). As a consequence, a weaker complex is formed in magnetized methanol solvent. To explain this behavior, we may consider the effect of a magnetic field treatment on a solvent and as a result upon the complexation process between the kryptofix 22DD and yttrium (III) ion.

Chang and Weng [26] investigated the effects of the magnetic field on the hydrogen-bonded structure of water. They found that the number of hydrogen bonds increased when the water passed through a magnetic field. Basically, various properties of water or aqueous solutions have a very close connection with the structure of water molecules. Liquid water forms a continuous network of hydrogen bonds because its molecules have two donors and two acceptor sites. The presence of spatial network of hydrogen bonds is the main property of the liquid water [27].

A lot of studies have been carried out to investigate the dependence of hydrogen bonding upon temperature in water [28, 29]. In general, the hydrogen bonding becomes weaker with increasing thermal motion of the atoms involved [30]. Hence, the water structure breaks down as the temperature increases. Normally the viscosity and dielectric constant of liquid water decrease as the temperature increases [31, 32]. It has been suggested that the effects of a magnetic field on water hydrogen bonds are similar with the effects of decreasing the temperature [33]. The theory of cluster models points out that the average size of water cluster decreases with increasing the temperature [34, 35]. Similar behavior has been also observed in the case of methanol molecules. It means that the hydrogen bond network in methanol molecules increases as the temperature decreases [36]. As a result, similar to the water, the viscosity and the dielectric constant of liquid methanol increase as the temperature decreases [32, 37]. This conclusion is in agreement with results obtained in this study.

The results obtained in this study show that when we use magnetized methanol solvent, the stability of the (kryptofix 22DD.Y)$^{3+}$ complex decreases. This can be related to the higher viscosity of the magnetized methanol solvent, which leads to a decrease in the rate of the complexation process between kryptofix 22DD and Y^{3+} cation in this extraordinary solvent compared to the non-magnetized methanol solvent. Furthermore, the higher dielectric constant of magnetized methanol solvent than that of the non-magnetized methanol solvent, leads to formation of a weaker complex in magnetized methanol solvent. It should be mentioned that the higher dielectric constant of magnetized methanol solvent can result in stabilization of the yttrium (III) cation and, therefore, leading to decrease the tendency of this cation to react with kryptofix 22DD and as a result the stability of the complex decreases.

As an attempt to get further insight about the complexation reaction, the stability constant of the (kryptofix 22DD.Y)$^{3+}$ complex was calculated and the corresponding results in both non-magnetized and magnetized methanol solvents are listed in Table 1. As is evident in Table 1, the stability constant of (kryptofix 22DD.Y)$^{3+}$ complex in non-magnetized methanol solvent is higher than that of the magnetized methanol solvent at all studied temperatures which corroborates the above contention.

Table 1 Log K_f values of (kryptofix 22DD.Y)$^{3+}$ complex in the non-magnetized and magnetized methanol solvents at different temperatures

Medium			Log $K_f \pm$ SD[a]	
(kryptofix 22DD.Y)$^{3+}$	15 °C	25 °C	35 °C	45 °C
Pure MeOH[b]	3.40 ± 0.03	3.65 ± 0.02	3.63 ± 0.02	3.30 ± 0.05
Pure MeOH[c]	2.89 ± 0.06	2.82 ± 0.14	2.74 ± 0.09	2.51 ± 0.10

[a] SD standard deviation

[b] In the absence of the magnetic field

[c] In the presence of the magnetic field

Conclusion

Since the solvent plays a critical role in local structure optimization and complex stabilization, and also in mechanism, kinetics and thermodynamics of complexation processes, we are interested to investigate the effect of solvent properties on complexation reactions of macrocyclic ligands with metal cations. In the present work, we studied the effect of non-magnetized and magnetized methanol solvents on the stability of (kryptofix 22DD.Y)$^{3+}$ complex at different temperatures using the conductometric method. We determined and compared the values of stability constant of (kryptofix 22DD.Y)$^{3+}$ complex in both non-magnetized and magnetized methanol solvents. The results obtained in this investigation show that the stability constant of the complex at different temperatures in magnetized methanol solvent is lower than that obtained in the case of non-magnetized methanol solvent. It seems that the changes of structure, viscosity and the dielectric constant of the methanol solvent under the influence of the magnetic field are probably effective in changing the (kryptofix 22DD.Y)$^{3+}$ complex stabilization in solution.

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