

Study of complex formation between La^{+3} , Ce^{+3} and Y^{3+} cations with some 18-membered crown ethers in methanol–water and methanol–acetonitrile binary mixtures

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Abstract The complexation reactions between some rare earth metal cations (Ln ; Y^{3+} , La^{3+} and Ce^{3+}) with 18-crown-6 (18C6), dicyclohexyl-18-crown-6 (DC18C6), benzo-18-crown-6 (B18C6) and decyl-18-crown-6 (Dec18C6), have been studied in methanol–acetonitrile (MeOH–AN) and methanol–water (MeOH– H_2O) binary mixtures using a competitive spectrophotometric method. 2-(2-thiazolylazo)-4-methyl phenol (TAC or L) was used as colorimetric complexant. It was found that the selectivity order of TAC for Ln cations is highly changed with changing the composition of the mixed solvents. Moreover, as the concentration of acetonitrile increases in MeOH–AN binary mixture, the stability of Ln–TAC complexes increases and passes through a maximum at a certain mole fraction of acetonitrile. In addition, the stability of Ln–crown ether complexes increases with increasing the concentration of methanol in MeOH– H_2O and acetonitrile in MeOH–AN binary solutions. A non linear behaviour was observed for variation of stability constants of all complexes versus the composition of the mixed solvents. The results show that 18C6 generally forms more stable complexes with La^{3+} and Ce^{3+} cations than DC18C6 in methanol and MeOH– H_2O binary mixtures, while this sequence is reversed in the methanol–acetonitrile binary mixtures which are rich with respect to acetonitrile.

Keywords Crown ethers · 2-(2-Thiazolylazo)-4-methyl phenol · La^{3+} , Ce^{3+} and Y^{3+} · Methanol–acetonitrile · Methanol–water · Spectrophotometry

Introduction

A substantial part of research works on macrocyclic polyethers have been devoted to their complexation with alkali, alkaline earth and somewhat to transition metal ions, but a little attention has been paid to lanthanide complexation and hence, information about the coordination behaviour of crown ethers towards the rare earth metal cations, is relatively scarce. Furthermore, such studies on lanthanide–crown ether complexation have been carried out in pure solvents and information in mixed solvents is very sparse.

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 [1, 2], as well as, their potential applications in fundamental and applied science [3–6] such as organic synthesis, bioorganic chemistry and homogeneous catalysis. Many of the applications of crown ether compounds are based on their complexing ability with various cations and hence, study of the stability of their complexes with metal cations and also the factors which affect their stability are important in many procedures such as separation, extraction, ion transport, chromatography and selectivity of analytical method. The stability constant of crown ether complexes has been determined by the use of different techniques such as potentiometry [7, 8], calorimetry [9, 10], conductometry [11–14], polarography [15, 16], NMR spectrometry [17, 18], spectrophotometry [19, 20]. It has

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been shown that the stability of lanthanide (III) complexes of crown ethers in solutions are distinctly changed and even in some cases prevented from formation of complexes and also thermodynamic behaviour of some of these complexes have been reversed by changing the solvent, the flexibility of the crown ether ring and also by the counter ion [21–27].

In previous work, we have used a competitive spectrophotometric method to study the complexation of some 15 and 18 membered crown ethers with La^{3+} , Ce^{3+} and Y^{3+} cations in MeOH to inspect the influence of various factors such as rigidity, substituent and ring size of the crown ethers and also the effect of pH on the stability of Ln–crown complexes [28]. In the present work, we used the above mentioned method with the same conditions to study the complexation of 18C6, DC18C6, B18C6, Dec18C6 and TAC ligand (Scheme 1) with La^{3+} , Ce^{3+} and Y^{3+} cations in MeOH– H_2O and MeOH–AN binary mixed solvents to inspect the influence of the ligand and the effect of binary mixed solvents on the stability and selectivity of the complexes formed between these cations and macrocyclic ligands.

Experimental

Reagents and apparatus

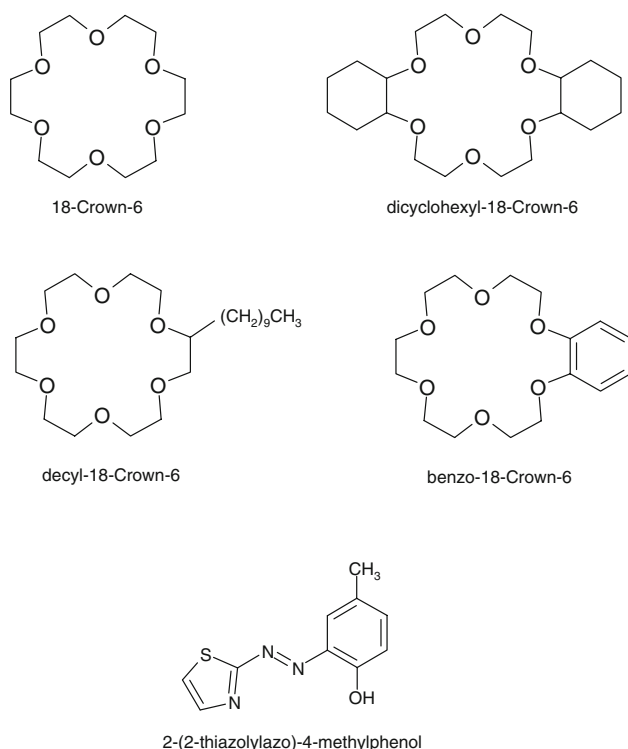
$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, DC18C6 (a mixture of *cis* and *trans*), B18C6, Dec18C6, hexamine, perchloric acid (all from

MERCK), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (PROLABO), $\text{Y}(\text{NO}_3)_3$ (PROLABO), with high purity were used without further purification. 2-(2-thiazolylazo)-4-methyl phenol (ALDRICH) with 99.9% purity was used as received. The methanol and acetonitrile (both from MERCK) with analytical grade and doubly distilled water were used as solvents. 18C6 (MERCK) was recrystallized from acetonitrile and dried under vacuum for 72 h at room temperature. All salts dried at 110 °C and hexamine dried at 80 °C in an oven for several hours. Perchloric acid and hexamine were used to maintain the pH at constant level. For each experiment, hexamine stock solution was freshly prepared just before use. Concentration of perchloric acid stock solution was determined by titration with NaOH titrisol (MERCK) in the presence of phenolphthalein indicator. The concentration of other stock solutions was determined from weight of dissolved amount of reagents.

A Shimadzu UV–Vis spectrophotometer 160 model was used for absorbance measurement in the 300–700 nm wavelength region. A match pairs of 1 cm quartz cell were used for all measurements. Before each experiment, the absorbance measurements were made over 200–800 nm wavelength region using empty pair cells to ensure that the two cells are match together. The volumetric apparatuses (pipette, micropipette, volumetric flask) were calibrated in usual manner by weighing the volume of distilled water to fill the apparatus to the mark at the desired temperature.

Procedure

The experimental procedure to obtain the formation constant of Ln–TAC and Ln–crown ether complexes is as follow: 3.5 mL of solution containing TAC ($2\text{--}4 \times 10^{-5}$ M), hexamine (0.01–0.04 M) and HClO_4 (0.0005–0.005 M) was placed in a quartz cell, then the metal cation solution was added in small increments (typically 50 μL) using a micro liter pipette to give concentration of Ln cation in the range of 4×10^{-5} – 6×10^{-4} M. Before and after each addition of cation solution, the absorbance of the solutions was measured at the peak wavelength (556–572 nm, depend on the solvent system) of Ln–TAC complex at 23 ± 0.5 °C. To the same solution, a solution of crown ether was further added in small increments to give concentration of crown ether from about 1×10^{-3} M to 3×10^{-2} M. After each addition, the absorbance of the solutions was again measured at the same wavelength. It was observed that the absorbance increases with increasing the concentration of the metal ions, but decreases with increasing the crown ethers concentration. Attainment of equilibrium for complexes was checked in a separated experiment by the observation of no further change in stabilized absorbance after 25 min.



Scheme 1

Results

The variation in absorption spectra of TAC solution at constant pH was recorded with addition of Ln cation and then followed by addition of crown ether at a constant C_{Ln} to confirm that only Ln-crown ether and 1:1 Ln-TAC complexes are formed in solution. A series of spectra of a buffered solution of TAC (3.2×10^{-5} M) in MeOH-H₂O binary mixture at various concentrations of La³⁺ cation (curves a–d), and different concentrations of 18C6 (curves e–g) are shown for example in Fig. 1. As seen from this figure, the absorption peak of free TAC at about 417 nm is indeed modified with addition of La³⁺ cation, so that an additional peak at longer wavelength (565 nm) appears upon complexation which corresponds to the presence of La-TAC complex and can be used as a basis for determination of the stability constants of La-TAC complexes. It is noteworthy, as seen in this figure, 2-(2-thiazolyazo)-4-methyl phenol and other reagents that are present in the solution do not absorb at the maximum wavelength of the complexes peak. Moreover, no protonated complexes of TAC may be formed due to simple acidic structure of this (monoprotic acid) reagent [20, 29], therefore, it has preference over the competitor reagents in this kind of studies.

The conditional stability constant of Ln-TAC complex is defined as:

$$K_{LnL'} = \frac{[LnL]}{[Ln][L']} \quad (1)$$

$$[L'] = [L] + [HL]$$

[LnL], [Ln], [L] and [HL] are molar concentration of Ln-TAC complex, lanthanide (III) cation, free TAC and protonated TAC, respectively (charges are omitted for simplicity). The $K_{LnL'}$ value was determined from slope to intercept ratio of the line based on Eq. (2) according to the Lang method [30]:

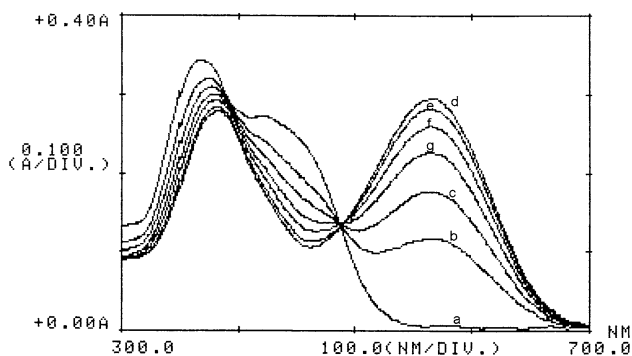


Fig. 1 Spectral changes of 3.3 mL solution of TAC (3.2×10^{-5} M) in MeOH-H₂O (mole% of MeOH = 64) at $C_{hex}/C_{HClO_4} = 0.01/0.001$, with addition (a) 0, (b) 20, (c) 40, (d) 220 μ L solution of La³⁺ (0.015 M) and further to (e) 30, (f) 180, (g) 350 μ L solution of 18C6 (0.25 M)

$$[C_{Ln}C_L/A] = \frac{(1/\epsilon_{LnL})[C_{Ln} + C_L - (A/\epsilon_{LnL})]}{+ (1/(K_{LnL'}\epsilon_{LnL}))} \quad (2)$$

The A and ϵ_{LnL} are the measured absorbance and molar absorptivity at peak wavelength of Ln-TAC complex, respectively. Moreover, C_{Ln} and C_L are the analytical concentration of Ln cation and TAC, respectively. Plots of $C_{Ln}C_L/A$ versus $C_{Ln} + C_L - (A/\epsilon_{LnL})$ in all cases were linear with a correlation coefficient of linearity larger than 0.999. A typical example of these plots, are shown in Fig. 2. It is should be noted that ϵ_{LnL} is assumed to be A_{max}/C_L and the reciprocal of the slope of this line yields the corrected value of ϵ_{LnL} which is utilized to replot the above relationship. The conditional stability constants (log K_f) of Ln-TAC complexes and also for La-TAC complex in different solvent systems and at various “ C_{hex}/C_{HClO_4} ” ratio are listed in Tables 1 and 2, respectively. The C_{hex} and C_{HClO_4} are the analytical concentration of hexamine and perchloric acid in solution, respectively.

The stability constants of 1:1 and 1:2 complexes of Ln-crown ethers are defined as:

$$K_{LnB} = \frac{[LnB]}{[Ln][B]} \quad (3)$$

$$K_{LnB_2} = \frac{[LnB_2]}{[Ln][B]^2} \quad (4)$$

Where [LnB], [LnB₂] and [B] denote the molar concentration of Ln-crown ether complex, Ln-(crown ether)₂ complex and free crown ether ligand, respectively.

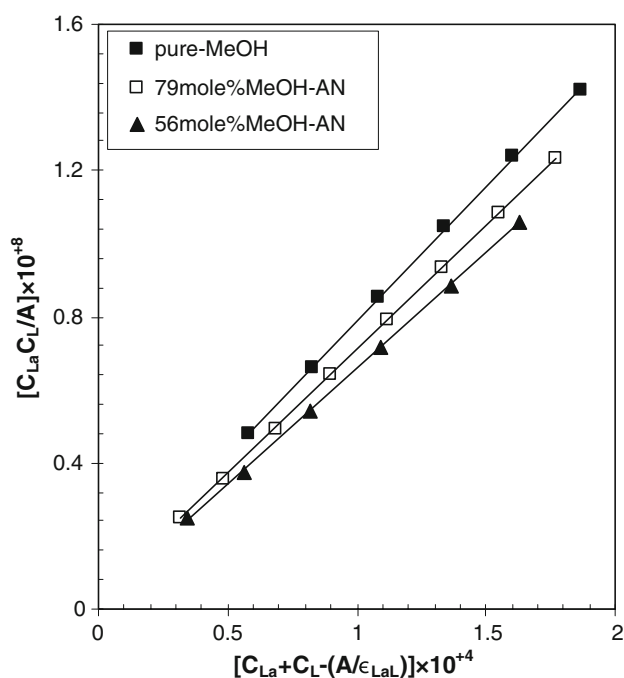


Fig. 2 Plots of $C_{Ln}C_L/A$ versus $C_{Ln} + C_L - (A/\epsilon_{LnL})$ for determination of conditional stability constants of La-TAC complexes in methanol and MeOH-AN binary mixtures (mole% of MeOH = 79 and 56) at $C_{hex}/C_{HClO_4} = 0.01/0.001$

Table 1 Conditional stability constants of Ln–TAC complexes in MeOH–AN and MeOH–H₂O binary mixtures

Medium ^c	C _{hex} /C _{HClO₄} ^b	Log K _f ± SD ^a		
		La–TAC	Ce–TAC	Y–TAC
30%MeOH–70%AN	0.01/0.001	5.40 ± 0.07	5.69 ± 0.07	5.28 ± 0.10
56%MeOH–44%AN		5.60 ± 0.11	5.94 ± 0.10	5.52 ± 0.09
79%MeOH–21%AN		5.33 ± 0.05	5.70 ± 0.10	5.70 ± 0.08
MeOH		5.08 ± 0.01	5.51 ± 0.01	5.62 ± 0.04
64%MeOH–36%H ₂ O		3.77 ± 0.02	4.20 ± 0.03	4.05 ± 0.05
40%MeOH–60%H ₂ O		3.09 ± 0.02	3.47 ± 0.04	3.35 ± 0.04
23%MeOH–77%H ₂ O		2.87 ± 0.03	3.39 ± 0.03	3.09 ± 0.05
H ₂ O		2.95 ± 0.03	3.21 ± 0.04	3.17 ± 0.03
64%MeOH–36%H ₂ O	0.02/0.0005	4.28 ± 0.02	4.69 ± 0.03	4.54 ± 0.05
40%MeOH–60%H ₂ O		3.60 ± 0.02	4.13 ± 0.03	3.86 ± 0.04
23%MeOH–77%H ₂ O		3.51 ± 0.03	4.06 ± 0.03	3.76 ± 0.05
H ₂ O		3.54 ± 0.04	4.06 ± 0.03	3.75 ± 0.04
64%MeOH–36%H ₂ O	0.02/0.001	3.89 ± 0.04		

^a SD = Standard deviation^b Ratio of analytical concentration of hexamine to perchloric acid^c The composition of solvent systems is expressed in mole percent of each solvent**Table 2** Stability constant (Log K_f) of La–TAC complex in different solvents at various “C_{hex}/C_{HClO₄}” ratios

Medium ^c	Log K _f ± SD ^a						
	C _{hex} /C _{HClO₄} ^b						
	0.01/0.0005	0.01/0.002	0.01/0.004	0.01/0.005	0.01/0.006	0.02/0.001	0.04/0.005
56%MeOH–44%AN		5.30 ± 0.10		4.99 ± 0.11	4.86 ± 0.10		
MeOH	5.68 ± 0.04	4.83 ± 0.05	4.67 ± 0.03		4.34 ± 0.03		
H ₂ O		2.62 ± 0.04				3.25 ± 0.04	2.81 ± 0.05

^a SD = Standard deviation^b Ratio of analytical concentration of hexamine to perchloric acid^c The composition of solvent systems is expressed in mole percent of each solvent

The conditional stability constant of Ln–TAC at a given analytical concentration of crown ether (C_B) and Ln cation (C_{Ln}), is defined as K_{Ln'L'} which its value can be determined from absorbance measurements based on Eq. (5) and it is related to C_B by Eq. (6). The details of calculation for obtaining Eqs. (5) and (6) have been described in reference [20].

$$K_{Ln'L'} = A / [(C_{Ln} - (A/\epsilon_{LnL})) (C_L \epsilon_{LnL} - A)] \quad (5)$$

$$(1/K_{Ln'L'}) = (1/K_{LnL'}) (1 + K_{LnB} C_B + K_{LnB_2} C_B^2) \quad (6)$$

At relatively low C_B or in the case of K_{LnB₂} = 0, Eq. (6) reduces to Eq. (7).

$$(1/K_{Ln'L'}) = (1/K_{LnL'}) + (K_{LnB}/K_{LnL'}) C_B \quad (7)$$

Plot of 1/K_{Ln'L'} versus C_B, yields straight line and the K_{LnB} value is determined from slope to intercept ratio of

this line or from product of slope in K_{LnL'} which was previously determined according to Eq. (2). We used the latter calculation due to less error. A typical example of these plots is shown in Fig. 3. Rearrangement of Eq. (6) yields, Eq. (8) that is used for determination of K_{LnB₂}.

$$\begin{aligned} & [(1/K_{Ln'L'}) - (1/K_{LnL'})] / C_B \\ & = (K_{LnB}/K_{LnL'}) + (K_{LnB_2}/K_{LnL'}) C_B \end{aligned} \quad (8)$$

When the formation of LnB₂ complexes occurs, the plot of the left side of Eq. (8) versus C_B yields a straight line and K_{LnB₂} value can be obtained from product of slope in K_{LnL'} value. The stability constants of the complexes formed between La³⁺ and Ce³⁺ cations with 18C6, DC18C6 and Dec18C6 in MeOH–AN and MeOH–H₂O binary mixtures, are listed in Table 3 and the results which are obtained for interactions between 18C6 with Y³⁺ and for B18C6 with La³⁺ cations are included in this table.

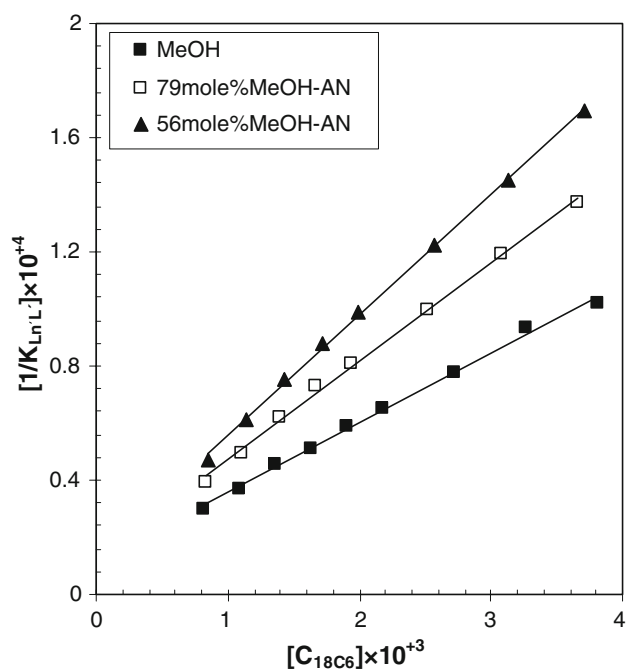


Fig. 3 Plots of $1/K_{LnL'}$ versus the analytical concentration of crown ether (C_{Crown}) to determine the stability constants of La-18C6 complexes in methanol and MeOH-AN binary mixtures (mole% of MeOH = 79 and 56) at $C_{hex}/C_{HClO_4} = 0.01/0.001$

Discussion

The hexamine has been used as a buffered constituent to fix the pH of slight acidic to neutral solutions in rare earth and transition metal cations complexation [31–33]. In our previous study [28], we showed that hexamine is a ligand with weak complexant strength in the lanthanide–crown ether complexation, and it is a suitable for buffer system.

Ohyoshi [34] has also reported that no complex formation occurs between hexamine and Eu^{3+} cation in the study of lanthanide complexation with murexide in aqueous solutions.

As seen in Fig. 1, all curves (a–g) have the same well defined isobestic point. This indicates that firstly, only a 1:1, La-TAC complex is formed and secondly, the dissociation of La-TAC complex only takes place with addition of 18C6 to a solution containing La^{3+} and TAC, therefore, La-18C6 complex is formed and ternary La-TAC-18C6 complex is not formed in solution. Similar results were obtained for other complexes in this study. In addition, as is shown for example in Fig. 2, an excellent linear relationship ($R > 0.999$) was observed for all of the plots of Ln-TAC complexes in all solvent systems which confirm again the formation of 1:1 complexes at defined conditions. Moreover, as it is shown in typical plots in Fig. 3, a good linear relationship is observed for La-18C6 complex in methanol and methanol–acetonitrile binary mixtures which indicates the formation of a 1:1 complex in solutions. Similar behaviour was observed for all other complexes of the crown ethers.

As seen from the data in Table 2 and also in Fig. 4, the value of stability constant of La-TAC complex depends on “ C_{hex}/C_{HClO_4} ” ratio. Similar behaviour was observed for other Ln-TAC complexes in all solvent systems. It is well known that the pH of solution increases with increasing “ C_{Hex}/C_{HClO_4} ” ratio and, therefore, $K_{LnL'}$ increases due to the side reaction: $H + L \rightleftharpoons HL$ [29]. In addition, as is evident from Fig. 5, when the concentration of methanol increases in MeOH– H_2O binary mixtures, the stability constants of Ln-TAC complexes first changes slowly to about 50 mole% of methanol and then increases rapidly.

Table 3 Stability constant (Log K_f) of Ln–crown ether complexes in MeOH-AN and MeOH- H_2O binary mixtures at $C_{hex}/C_{HClO_4} = 0.01/0.001$ M

Complex	Log $K_f \pm SD^a$							
	MeOH-AN mixtures ^c				MeOH- H_2O mixtures ^c			
	30%MeOH	56%MeOH	79%MeOH	MeOH	64%MeOH	40%MeOH	23%MeOH	
La-18C6	4.70 ± 0.09	3.91 ± 0.05	3.78 ± 0.06	3.54 ± 0.03	1.95 ± 0.03	1.38 ± 0.04	1.00 ± 0.05	
La-DC18C6	5.24 ± 0.15	3.92 ± 0.04	3.51 ± 0.06	2.80 ± 0.03	1.80 ± 0.03	1.36 ± 0.03	1.11 ± 0.05	
Ce-18C6	4.29 ± 0.17	3.54 ± 0.07	3.46 ± 0.07	3.09 ± 0.04	1.98 ± 0.04	1.59 ± 0.05	1.45 ± 0.05	
Ce-DC18C6	4.92 ± 0.15	3.70 ± 0.09	3.36 ± 0.11	2.68 ± 0.04	1.84 ± 0.04	1.34 ± 0.05	1.26 ± 0.05	
La-Dec18C6	4.19 ± 0.11	4.07 ± 0.08	3.88 ± 0.15	3.46 ± 0.06				
Ce-Dec18C6	4.25 ± 0.10	4.14 ± 0.07	3.94 ± 0.11	3.32 ± 0.06				
La-B18C6	–	d	d	d				
Y-18C6	d	d	d	d				

^a SD = Standard deviation

^b Ratio of analytical concentration of hexamine to perchloric acid

^c The composition of solvent systems is expressed in mole percent of the solvent

^d No complex is formed in solution

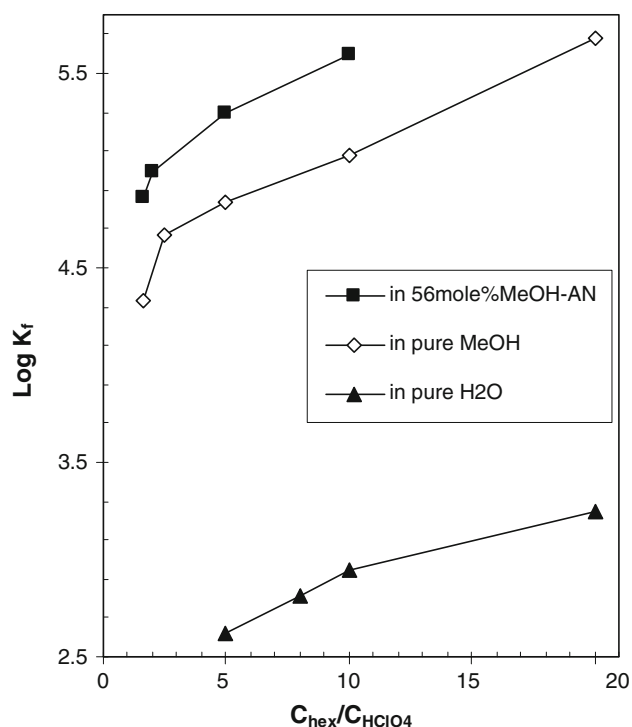


Fig. 4 Changes of stability constant of La-TAC complex versus “ $C_{\text{hex}}/C_{\text{HClO}_4}$ ” ratio in different solvents

This behaviour is very similar to those which are observed for Ln-crown ether complexes in MeOH–H₂O binary solutions. As is evident from Table 1, the selectivity order of TAC for Y³⁺, La³⁺ and Ce³⁺ cations in methanol under identical conditions is: Y³⁺ > Ce³⁺ > La³⁺ which is in agreement with the reported results by Ohyoshi and Kohata [20] who have pointed out that as the size of lanthanide cation decreases, the charge density on cation increases and, therefore, the interactions of the cation with this chelate become stronger. But the selectivity sequence of TAC for these metal cations in MeOH–H₂O binary mixtures is: Ce³⁺ > Y³⁺ > La³⁺. It seems that the interactions of solvent molecules with Y³⁺ are stronger than Ce³⁺ cation in water–methanol binary solutions than in methanol and, therefore, the selectivity order of TAC for these two cations is reversed in the mixed solvent.

The changes of the stability constants ($\log K_f$) of Ln-TAC complexes versus the mole fraction of acetonitrile in MeOH–AN binary mixture are shown in Fig. 6. As seen in this figure, with increasing the acetonitrile concentration in MeOH–AN binary mixture, the stability of La-TAC and Ce-TAC complexes initially increases and then decreases at about 0.5 mole fraction of acetonitrile. Similar behaviour is observed for Y-TAC complex, but its stability decreases from about 0.25 mole fraction of acetonitrile in this binary system. It seems that at high concentration of methanol in MeOH–AN binary solutions, the preferential solvation of

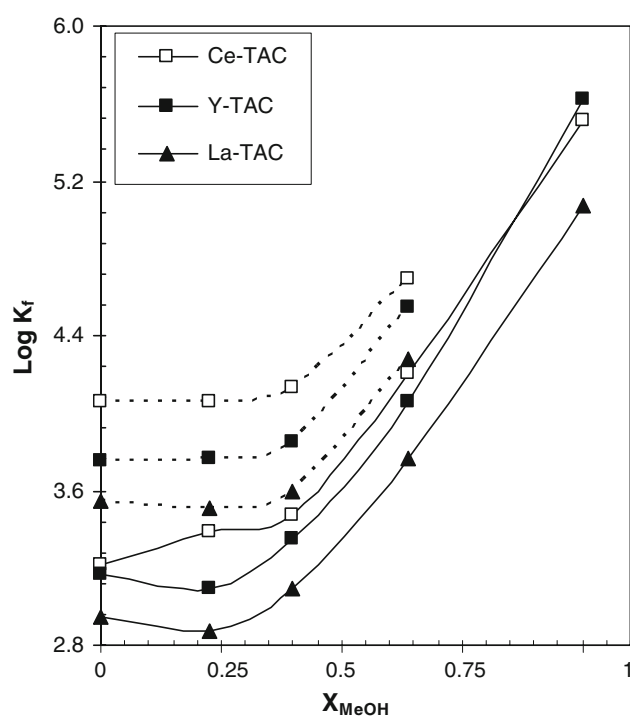


Fig. 5 Changes of stability constant of Ln-TAC complexes with the composition of MeOH–H₂O binary mixture at $C_{\text{hex}}/C_{\text{HClO}_4} = 0.01/0.001$ M (solid line —), and at $C_{\text{hex}}/C_{\text{HClO}_4} = 0.02/0.0005$ M (dotted line - - -)

the metal cations is a dominant factor in complexation reactions, but as the concentration of methanol decreases in solutions, the effect of interactions between the counter ion and the Ln cations becomes important in complexation processes. It is known that the counter ion associates with Ln³⁺ cations to some degree in solutions [35, 36]. Since the acceptor number of acetonitrile (18.9) is smaller than that of methanol (41.3), the solvation of the counter ion is weaker in AN than that of MeOH and, therefore, the interactions of these metal cations with the counter ion becomes stronger as the concentration of acetonitrile increases in MeOH–AN binary solutions.

The selectivity order of TAC for Ln cations in an acetonitrile–methanol solution (mole% of MeOH = 79) at the same conditions is: Y³⁺ \approx Ce³⁺ > La³⁺, but in the case of other MeOH–AN binary mixed solvents (mole% of MeOH = 56 and 30) is: Ce³⁺ > La³⁺ > Y³⁺.

As seen in Figs. 7 and 8, the complexation reactions between La³⁺ and Ce³⁺ cations with 18C6, DC18C6 and Dec18C6 are sensitive to the solvent composition so that the stability of all complexes increases with increasing the methanol concentration in MeOH–H₂O binary solutions and also with increasing the concentration of acetonitrile in MeOH–AN binary mixtures. A non-linear behaviour is observed for changes of the stability constants of all complexes versus the composition of the mixed solvents. In

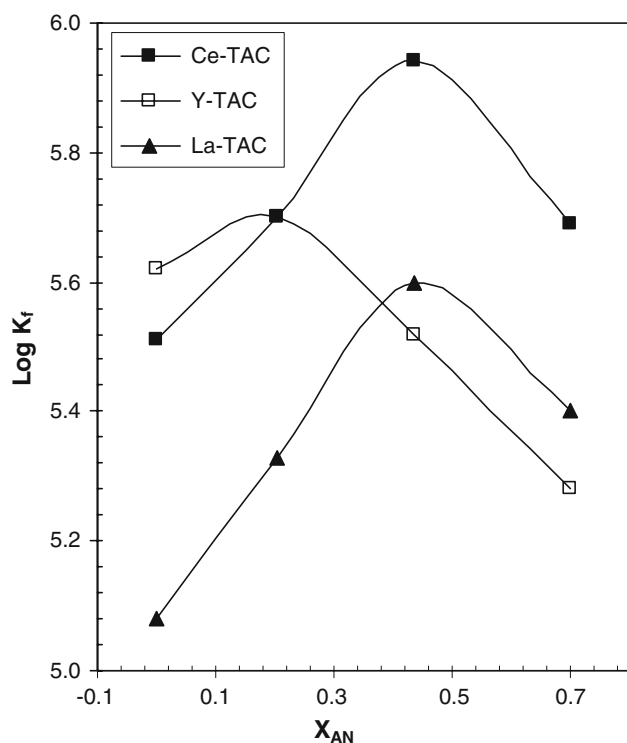


Fig. 6 Changes of stability constant of Ln-TAC complexes with the composition of MeOH-AN binary mixture at $C_{\text{hex}}/C_{\text{HClO}_4} = 0.01/0.001$

the cases of Ln-crown ether complexes in MeOH-H₂O binary mixture (Fig. 7), the stability constants (Log K_f) initially increase slowly to about 0.5 mole fraction of methanol and then increase more rapidly until the mole fraction of methanol is reached to 1. This behaviour may be attributed to the preferential solvation of lanthanide (III) cations by water molecules. Water with a high donor number (DN = 33) solvates the metal cations much more strongly than methanol (DN = 19) molecules. Moreover, the solvent-solvent interactions between water and methanol molecules in their binary solutions may be responsible for the non-linear relationship between the log K_f of the complexes and the composition of the MeOH-H₂O binary mixture. Similar behaviour has been observed for PhN15C5-Ag⁺ complex in MeOH-H₂O solutions [12]. Mashima et al. [37] have reported that some of the physical properties of MeOH-H₂O binary mixture show a maximum in certain composition.

As seen in Table 3, the stability constant of complexes of La³⁺ cation with 18C6 and DC18C6 is generally larger than Ce³⁺ cation in methanol-acetonitrile binary mixtures. Similar behaviour has been observed in methanol solutions [28]. In addition, as illustrated in Fig. 8, the 18C6 forms more stable complexes with La³⁺ and Ce³⁺ cations in methanol solution than DC18C6, but a reverse trend is observed in MeOH-AN binary mixtures which are rich in acetonitrile.

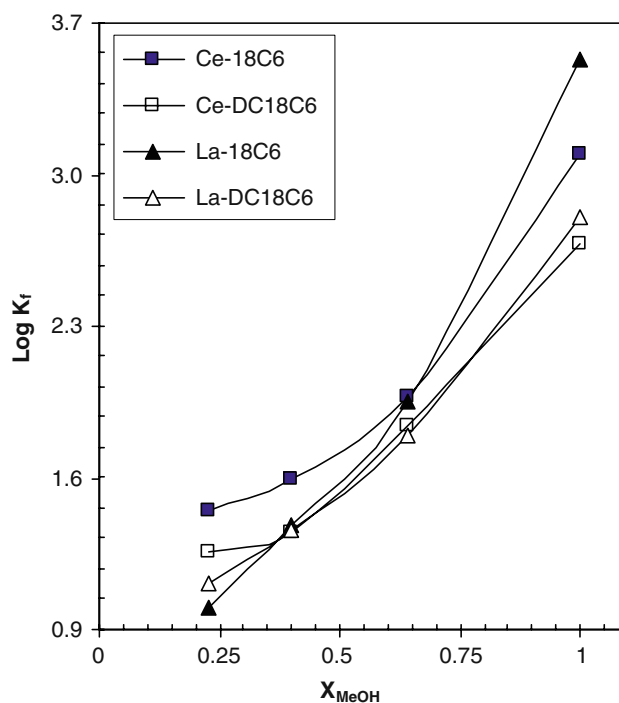


Fig. 7 Changes of stability constant of Ln-crown ether complexes with the composition of MeOH-H₂O binary mixture at $C_{\text{hex}}/C_{\text{HClO}_4} = 0.01/0.001$

Since the lanthanide (III) cations have high charge, small size and high coordination number [35, 38–45], therefore, they are capable to form complexes with crown ethers in which the complexation are accompanied by various types of interactions and hence, they show different and some contradictory behaviour in complexation with these macrocyclic ligands. These observations suggest that a delicate balance among ligand-cation binding, the interaction of anions or other donor species with free and complexed cation, solvation events, and the ligand conformational change, determine the stability of these complexes in solution. The results obtained in this work and also our previous results indicate that the conformational change of the ligand is probably a dominant factor in Ln-crown ether complexation [28].

One possible explanation for the higher stability constants of 18C6 complexes with La³⁺ and Ce³⁺ cations than those of DC18C6 in methanol and methanol-water binary mixtures is due to the presence of the cyclohexyl groups in DC18C6 which results in an unfavourable conformation of this ligand in its complexation process with these metal cations with respect to 18C6. As is evident from Table 3 and Fig. 8, the stability of DC18C6 complexes with La³⁺ and Ce³⁺ cations are larger than those of 18C6 in MeOH-AN binary mixtures which are rich in acetonitrile (mole% of AN > 44%). It is known that the 18C6 forms a more stable complex with acetonitrile molecules in compared

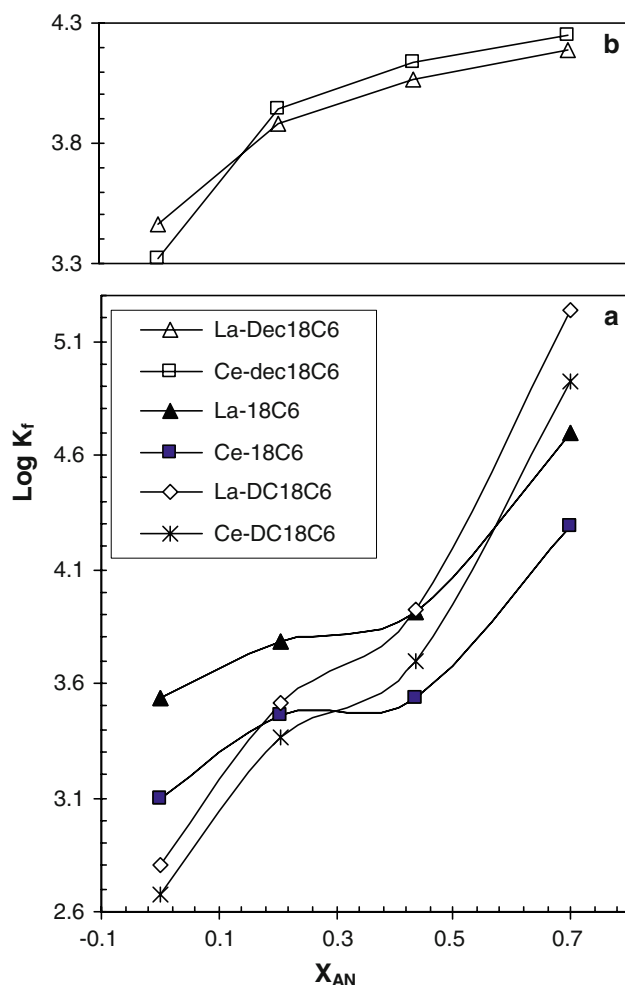


Fig. 8 Changes of stability constant of Ln-crown ether complexes ((a): complexes of 18C6 and DC18C6, (b): complexes of Dec18C6) with the composition of MeOH-AN binary mixture at $C_{\text{hex}}/C_{\text{HClO}_4} = 0.01/0.001$

with many other crown ethers [46–50], therefore, the interaction between 18C6 and acetonitrile increases with increasing the acetonitrile concentration in MeOH-AN binary mixture, which results in formation of weaker complexes between La³⁺ and Ce³⁺ cations with this macrocyclic ligand compared with DC18C6 in these solvent systems. As is obvious from Table 3, B18C6 does not form any complex with La³⁺ cation in methanol and MeOH-AN binary mixtures. Since the phenyl group substituent on the ring of this crown ether, induces a large rigidity on the ligand, therefore, it seems that the unfavourable conformational change of the ligand prevents the formation of complex in solution. Previous studies have also shown that the DB18C6 does not form any stable complex with La³⁺ and Ce³⁺ cations in methanol solutions [27].

The results obtained for complexation of Y³⁺ cation with 18C6 in methanol and methanol-acetonitrile binary

solutions (Table 3), show that there is no significant interaction between Y³⁺ cation and this macrocyclic ligand. Since Y³⁺ cation is much smaller than La³⁺ and Ce³⁺ cations, it interacts with the solvent molecules and the counter ion more strongly than the other two metal cations and, therefore, the Y³⁺ cation form a weaker complex with 18C6 than those of La³⁺ and Ce³⁺ cations in these solutions.

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