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A Spectrophotometric Study of Complex Formation of Y^{3+}, La^{3+} and Ce^{3+} with Some 18- and 15-Membered Crown Ethers in Methanol

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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), decyl-18-crown-6 (Dec18C6), benzo-18-crown-6 (B18C6), benzo-15-crown-5 (B15C5) and N-phenylaza-15-crown-5 (PhN15C5) have been studied in methanol using a competitive spectrophotometric method. 2-(2-Thiazolylazo)-4-methyl phenol (TAC or L) was used as colorimetric complexant and the pH of solutions was fixed by hexamine/perchloric acid buffered system. The results show that the behaviour and stability of Ln-crown ether complexes are strongly affected by ring size, flexibility and substituent of crown ether ring, so that the complexes of 18C6 and DC18C6 with La^{3+} and Ce^{3+} cations are formed as 1:1, while those of Dec18C6 are formed as 1:2 in addition to 1:1 stoichiometry. Moreover, no evidence was observed for the interaction between B18C6, B15C5 and PhN15C5 with these cations in methanol solutions. It was found that the stability of Ln-crown ether as well as Ln-TAC complexes depends on pH of the solution. The stability constants of Ln-TAC complexes increase with increasing hexamine/perchloric acid concentration ratio, but in the case of Ln-crown ether complexes decrease. In addition, the results show that the complexation of Y^{3+} cation with all of the crown ethers is inappreciable in this solution.

Key Words: Crown ether, 2-(2-Thiazolylazo)-4-methyl phenol, La^{3+}, Ce^{3+}, Y^{3+}, Methanol, Spectrophotometry.

INTRODUCTION

Most of the research works on macrocyclic polyethers have been focused on alkali, alkaline earth and on transition metal cations but a little attention has been paid to lanthanide complexation. 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 spectroscopy as well as their potential applications in fundamental

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and applied science such as organic synthesis, bioorganic chemistry and homogeneous catalysis[1-6]. Many applications of crown ether compounds are based on their complexing behaviour with various cations and hence the stability constants of their complexes and follow the factors which affect their stability are important in many procedures such as separation, extraction, ion transport, chromatography and improvement the selectivity of analytical method. The stability constant of crown ether complexes has been determined by 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].

In the present work, the competitive spectrophotometric method is used to study the complexation of several 18 and 15-membered crown ethers with La^{3+}, Ce^{3+} and Y^{3+} cations in methanol in order to inspect the influence of various factors such as rigidity, ring size and substituent of the crown ether and also the pH effects on the stability of various Ln-crown ether complexes under identical conditions.

EXPERIMENTAL

$La(NO_3)_3{\cdot}6H_2O$, DC18C6 (a mixture of *cis* and *trans*), Dec18C6, B18C6, B15C5, PhN15C5, hexamine, perchloric acid, tetraethylammonium chloride (all from Merck), $Ce(NO_3)_3{\cdot}6H_2O$ (Prolabo), $Y(NO_3)_3$ (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 with analytical grade was used as solvent. 18C6 (Merck) was recrystallized from acetonitrile (Merck) and dried under vacuum for 72 h at room temperature. All the salts dried at 110 °C and hexamine dried at 80 °C in an oven for several hours. Tetraethylammonium chloride was used to adjust the ionic strength of solution at 0.02. Perchloric acid and hexamine were used to maintain the pH at constant level. For each experiment, hexamine stoke 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 the weight of dissolved amount of reagents.

A Shimadzu UV-Vis spectrophotometer 160 model was used for absorbance measurements in the 300-700 nm wavelength regions. 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 cell to ensure that two cells match together. A Hanna pH meter 213 model was used for pH measurements. The volumetric apparatus (pipette, micropipette, volumetric flask) were calibrated in usual way by weighing the volume of distilled water to fill the apparatus to the mark at the defined temperature.

Procedure: The experimental procedure to obtain the conditional formation constants of Ln-TAC and Ln-crown ether complexes is as follow: 3.5 mL of a solution containing 2-(2-thiazolylazo)-4-methyl phenol (TAC) (2-3 × 10^{-5} M), hexamine (0.01-0.02 M) and $HClO_4$ (0.0005-0.012 M) at constant ionic strength, 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 that increased from about 4 × 10^{-5} to 6 × 10^{-4} M. Before and after each addition of cation, the absorbance of the solutions was measured at the peak wavelength (572 nm) 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 that increased from about 1 × 10^{-3} 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 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 the stabilized absorbance after 25 min. To ensure that pH of the solution has been maintained fixed in each experiment, an identical procedure was performed in water and no significant change was monitored by pH meter.

RESULTS AND DISCUSSION

The variation in absorption spectra of 2-(2-thiazolylazo)-4-methyl phenol (TAC) solution at constant pH and ionic strength was recorded with addition of Ln cation and follow with 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 (2.66 × 10^{-5} M) TAC solution in MeOH at various concentration of La^{3+} cation (curves b-d) and different concentration of 18C6 (curves e-g), are shown in Fig. 1. As seen from this figure, the absorption peak of free TAC at about 420 nm is indeed modified with addition of La^{3+} cation so that the additional peak at longer wavelength (572 nm) appear upon complexation which correspond 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 that 2-(2-thiazolylazo)-4-methyl phenol and other reagents which are present in the solution do not absorb at the maximum wavelength of the complexes peak.

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

$$K_{LnL'} = [LnL]/[Ln]\,[L'] \tag{1}$$

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

[LnL], [Ln], [L] and [HL] are the molar concentration of Ln-TAC complex, lanthanide(III) cation, free TAC and protonated TAC, respectively (charge are omitted for simplicity). The $K_{LnL'}$ values were determined from the slope ($1/\varepsilon_{LnL}$) to intercept ($1/(K_{LnL}\cdot\varepsilon_{LnL})$) ratio of the line based on eqn. 2 according to Lang method[21].

$$\{C_{Ln}C_L/A\} = (1/\varepsilon_{LnL})\,\{C_{Ln} + C_L - (A/\varepsilon_{LnL})\} + (1/(K_{LnL}\cdot\varepsilon_{LnL})) \tag{2}$$

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^{3+} and TAC ligand, respectively. The plots of $C_{Ln}C_L/A$ *vs.* $C_{Ln} + C_L - (A/\varepsilon_{LnL})$ in all cases were linear with a correlation coefficient of linearity larger than 0.9999. A typical example of these plots, are shown in Fig. 2. It is noticeable that ε_{LnL} is assumed to be A_{max}/C_L and reciprocal of the slope of this line yields the corrected value of ε_{LnL} which was utilized to replot above relation. The conditional stability constants (log K_f) for Ln-TAC complexes at various C_{hex}/ C_{HClO_4} ratio in methanol solutions are listed in Table-1. The C_{hex} and C_{HClO_4} are the analytical concentration of hexamine and perchloric acid, respectively.

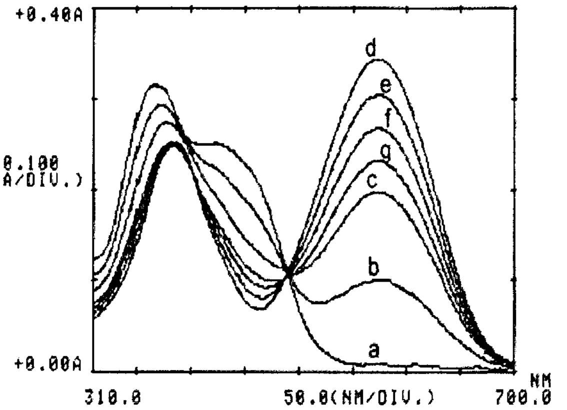

Fig. 1. Spectral changes of 3.4 mL solution of TAC (2.66 × 10^{-5} M) at C_{hex}/C_{HClO_4} = 0.01/ 0.001, with addition (a) 0, (b) 10, (c) 25, (d) 175 μL solution of La^{3+} (0.0036 M) and further to (e) 100, (f) 200 (g) 350 μL solution of 18C6 (0.0256 M)

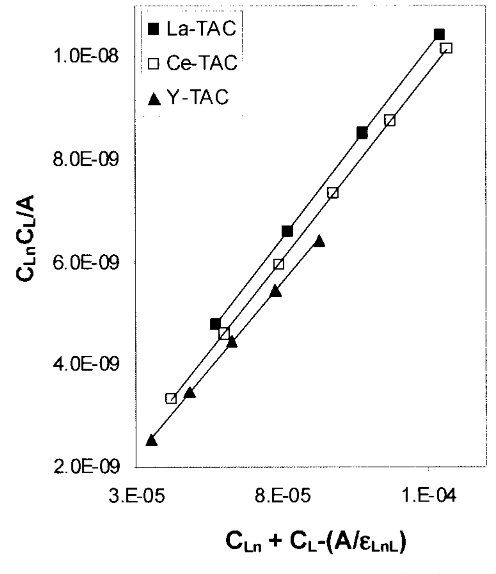

Fig. 2. Plots of $C_{Ln}C_L/A$ *vs.* $C_{Ln} + C_L\text{-}(A/\varepsilon_{LnL})$ for determination of conditional stability constants of Ln-TAC complexes in methanol at C_{hex}/C_{HClO_4} = 0.01/0.001

TABLE-1
CONDITIONAL STABILITY CONSTANTS OF Ln-TAC COMPLEXES IN METHANOL AT 23 °C

C_{hex}/C_{HClO4}[b]	log K_f ± SD[a]		
	La-TAC	Ce-TAC	Y-TAC
0.01/0.0080	4.25 ± 0.05	–	–
0.01/0.0060	4.34 ± 0.03	–	–
0.01/0.0040	4.67 ± 0.03	–	–
0.01/0.0020	4.83 ± 0.05	–	–
0.01/0.0010	5.08 ± 0.01	5.51 ± 0.01	5.62 ± 0.04
0.01/0.0005	5.68 ± 0.04	–	–
0.02/0.0120	4.32 ± 0.01	4.65 ± 0.04	–

[a] SD = Standard deviation.

[b] C_{hex}/C_{HClO4} = Ratio of analytical concentration of hexamine to perchloric acid.

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

$$K_{LnB} = [LnB] / [Ln]\,[B] \qquad (3)$$

$$K_{LnB2} = [LnB_2] / [Ln]\,[B]^2 \qquad (4)$$

where [LnB], [LnB$_2$] and [B] denote the molar concentration of Ln-crown, Ln(crown)$_2$ and free crown ether, respectively. The conditional stability constant of Ln-TAC at a given analytical concentration of crown ether (C_B) is defined as $K_{Ln'L'}$, its value can be determined from absorbance measurements based on eqn. 5 and it is related to C_B by eqn. 6. The details of calculation for obtaining eqns. 5 and 6 have been described as reported[20].

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

$$(1/K_{Ln'L'}) = (1/K_{LnL'})\,(1 + K_{LnB}C_B + K_{LnB2}C_B^2) \qquad (6)$$

In the cases of $K_{LnB2} = 0$ or at relative low C_B, eqn. 6 reduces to eqn. 7.

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

Plot of $1/K_{Ln'L'}$ *vs.* C_B yields a 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 eqn. 2. We used the latter calculation due to less error. A typical example of these plots, are shown in Fig. 3. Rearrangement of eqn. 6 yields eqn. 8 that was used for determination of K_{LnB2}.

$$[(1/K_{Ln'L'})-(1/K_{LnL'})]/C_B = (K_{LnB}/K_{LnL'}) + (K_{LnB2}/K_{LnL'})\,C_B \qquad (8)$$

When the formation of LnB$_2$ occurs, the plot of the left side of eqn. 8 *vs.* C_B at relatively high C_B values yields a straight line and K_{LnB2} value can be obtained from product of slope in $K_{LnL'}$ value. The equilibrium constants of complexation reaction between La^{3+} and Ce^{3+} cations with 18C6, DC18C6 and Dec18C6 at various C_{hex}/C_{HClO4} ratios in methanol are listed in Table-2. The results obtained for interaction between Y^{3+} and La^{3+} cations with 18C6, B18C6, B15C5 and PhN15C5 are also included in this Table.

As seen in Fig. 1, all curves (a-g) have the same well defined isobestic point. This indicates that firstly, only 1:1 La-TAC complex is formed in solution and secondly, the dissociation of La-TAC complex only take place with addition of 18C6 to solution containing La^{3+} and TAC, therefore La-18C6 complex is formed, but ternary La-TAC-18C6 complex is not formed in solution. Similar results were obtained for other complexes in this study. Moreover, as seen in Fig. 2, an excellent linearity relation ($r > 0.9999$) was observed for all the plots of Ln-TAC complexes which confirms again the formation of 1:1 complexes at defined conditions. In addition, as it is shown for a typical plots in Fig. 3, a good linear relationship ($r > 0.99$) is observed for complexes of 18C6 and DC18C6 except of Dec18C6 at wide range of crown ether concentrations and hence this indicates that only 1:1 complexes of La^{3+} and Ce^{3+} with 18C6 and DC18C6 are formed in solutions. In the case of Dec18C6 complexes, two linear regions with good linearity relations were observed, one at low concentration range of crown ether according to eqn. 7 and another at high concentration of crown ether based on eqn. 8. The K_{LnB} and K_{LnB2} values were determined based on related lines as mentioned above.

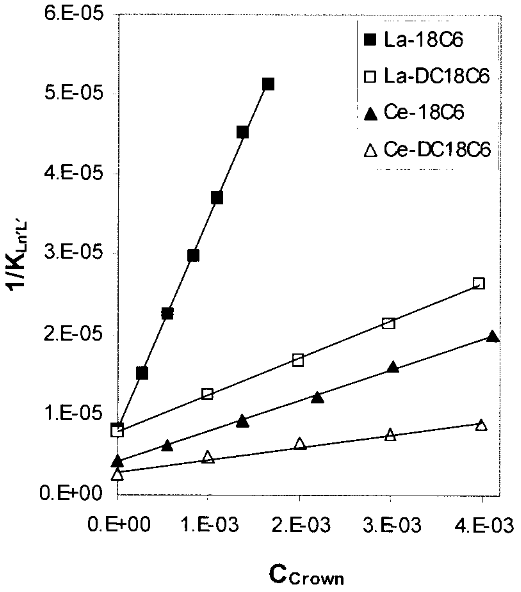

Fig. 3. Plots of $1/K_{Ln'L'}$ *vs.* C_{crown} to determine the stability constants of Ln-crown complexes in methanol at $C_{hex}/C_{HClO4} = 0.01/0.001$

As shown in Table-1, log K_f values for La-TAC complex are equal at 0.02/0.012 and 0.01/0.006 M of C_{hex}/C_{HClO4} ratios which indicate that the stabilities of La-TAC complexes are independent of absolute value of C_{hex} and therefore, hexamine is an inert reagent and is suitable for buffer system. Ohyoshi[22] has also reported that no complex formation occurs between hexamine and lanthanide(III) cation in study of lanthanide complexation with murexide in aqueous solution and hence pointed out that hexamine is a ligand with weak complexing behaviour. On the other hand, as seen in Table-1 and Fig. 4, the stability constant of La-TAC complex depend on C_{hex}/C_{HClO4} ratio. It is well known that the pH of solutions increases with increasing C_{Hex}/C_{HClO4} ratio and, therefore, $K_{LnL'}$ increases due to the side reaction, $H + L \rightleftharpoons HL$[23]. In addition, as is evident from Table-1, the selectivity order of TAC for Ln cations in identical conditions is: $Y^{3+} > Ce^{3+} > La^{3+}$. This is in agreement with reported results of Ohyoshi[20] who has found out that as the size of lanthanide cation decreases, the charge density on cation increases and therefore, interaction of cation with chelates become stronger.

TABLE-2

log K_f ± SD VALUES FOR Ln-CROWN COMPLEXES IN METHANOL AT 23 °C

Cation	Ligand	C_{hex}/C_{HClO4}	Present work	Other works
La^{3+}	18C6	0.01/0.008	3.94 ± 0.01	3.89 ± 0.08[b]
		0.02/0.012	3.81 ± 0.01	
		0.01/0.004	3.76 ± 0.03	
		0.01/0.001	3.54 ± 0.03	
		0.01/0.0005	3.37 ± 0.03	3.29 ± 0.03[c]
	DC18C6	0.02/0.012	3.56 ± 0.04	
		0.01/0.001	2.80 ± 0.03	
	Dec18C6	0.01/0.001	3.46 ± 0.06 6.79 ± 0.09[a]	
	B18C6	0.02/0.012	[d]	
	B15C5	0.02/0.012	[d]	
	PhN15C5	0.02/0.012	[d]	
Ce^{3+}	18C6	0.02/0.012	3.44 ± 0.04	3.67 ± .05[b]
		0.01/0.001	3.09 ± 0.04	
	DC18C6	0.02/0.012	3.11 ± 0.04	
		0.01/0.001	2.68 ± 0.04	
	Dec18C6	0.01/0.001	3.32 ± 0.06 7.25 ± 0.08[a]	
Y^{3+}	18C6	0.02/0.012	[d]	
		0.01/0.001	[d]	
	B15C5	0.02/0.012	[d]	

[a]The value of log β_2 for (1:2) Ln-(crown)$_2$ complex, [b]Reference 20, [c]Reference 24, [d]No complex is formed in the solution.

Two features in the stability of Ln-Crown complexes were studied in present work, are particularly significant, (i) the effect of cation size, rigidity of crown ether, size and substituents of crown ring, (ii) the $HClO_4$ concentration effect. These may be rationalized as follow:

I: As is evident from Table-2, the La^{3+} and Ce^{3+} cations form stable complexes with 18C6 and DC18C6 as 1:1 stoichiometry and with Dec18C6 as 1:2 in addition to 1:1 stoichiometries, but they do not form complexes with B18C6 and 15-membered crown ethers. Under identical conditions, the selectivity sequence for the formation of 1:1 complexes with La^{3+} is: 18C6 ≈ Dec18C6 > DC18C6 and for Ce^{3+}: Dec18C6 > 18C6 > DC18C6. No evidence was observed for formation a complex between Y^{3+} cation and crown ethers in absorbance measurements.

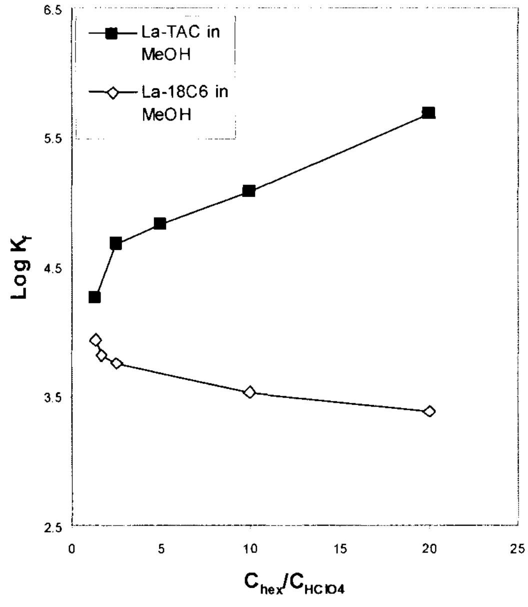

Fig. 4. Variation of stability constants of La-TAC and La-18C6 complexes *vs.* C_{hex}/C_{HClO_4} ratio in methanol

The thermodynamic parameters which are available[24] for complexation of lanthanide cations with 18-crown-6 in methanol solvent show that these complexes are stabilized by entropic effect, but destabilized by enthalpy effect. This suggest that the small and high charged cations such as Ln^{3+} are strongly solvated[25,26] so that much energy is expanded in desolvation step and hence the enthalpy change is positive, but the entropy contribution from loss of solvent molecules causes the complexation to be favoured[24]. On the contrary to methanol solvent, these complexes are enthalpy stabilized, but entropy destabilized in acetonitrile[27]. In addition, the complexation of small cations such as Ln^{3+} with 18-membered crown ethers in which the cavity size of these ligands (2.6-3.2 Å) are much larger than cation sizes (1.88-2.12 Å), take place with a conformational change of the ligands. These observations indicate that the delicate balance among ligand-cation binding, solvation events and ligand conformational change factors determine the stability of these complexes.

As is evident from Table-2, among crown ethers which were used in this study, 18C6 generally form the most stable complexes with Ln^{3+} cations in methanol while

DC18C6 in spite of two cyclohexyl substituant groups that increases donor strength of ligand, it form a less stable complex than 18C6. Since 18C6 is more flexible than DC18C6 and B18C6. It seems that a favourable conformation of complexed ligand results in a suitable orientation of donor atoms toward Ln^{3+} cations and less strained conformation of crown ether, is one of important factors in complexation of crown ether with Ln^{3+} in methanol solutions. For this reason, as seen in Table-2, the equilibrium constants value for complexation of La^{3+} and Ce^{3+} cations with DC18C6 (a more rigid ligand) are much less than those with 18C6. In addition, due to presence of a phenyl group on the ring of B18C6 which induces a large rigidity on ligand, it does not form any complex with La^{3+} cation in solution. It is noticeable that the stability of lanthanide-crown complexes in acetonitrile are similarly affected by flexibility of the ligand, so that the attachment of substituent groups on 15C5[28-30] or 18C6[27,31] rings reduces the stability of related complexes. It is interesting to note, on the contrary to 18C6 and DC18C6, the Dec18C6 form stable complexes with La^{3+} and Ce^{3+} cations as 1:2 in addition to 1:1 stoichiometry. Although there are no reports on complexes of Dec18C6 with lanthanide cations in solution but the reported results show that 18C6[20,24,27,32], DB18C6[31,33] and Di-*tert*-butylbenzo-18C6[34], form complexes with lanthanide(III) cations as 1:1 stoichiomety in solutions while 1:2 in addition to 1:1 stoichiomety, was observed for Ln-15C5 and Ln-12C4 complexes in some cases[35,36]. It seem, Dec18C6 due to existence of large chain alkyl substituent, having a favourable conformation in their complexes so that it can not all-around incorporated the Ln^{3+} cation and is forced to coordinate with lanthanide in out-of-cavity fashion and hence this ligand is capable to form 1:2 stoichiometry complexes. The results (Table-2) show that the stability constants values of La-crown in all cases are larger than those of Ce-crown complexes and this is in agreement with the reported results by Ohyoshi *et al.*[20]. One possible explanation for this sequence may be attributed to the size of cation which affects the solvation phenomena of cation and conformational change of ligand.

As illustrated in Table-2, B15C5 and PhN15C5 do not form stable complexes with Ln^{3+} cations in methanol solutions, although their cavity sizes (1.7-1.9 Å) are close to lanthanide cations size (1.88-2.12 Å). It seems that the less flexibility of 15-crown ethers results in unfavourable conformation of complexed ligand accompany with difficulty of cation desolvation, are responsible for weak interaction between these crown ethers with La^{3+} cation. The results obtained for complexation of Y^{3+} with 18C6 and B15C5 (Table-2), show that there is no significant interaction between Y^{3+} cation and these macrocyclic ligands in methanol solutions. Since Y^{3+} cation is much smaller than lanthanide(III) cations, it is more solvated in methanol solution, therefore, this factor and probably the unfavourable conformational change of ligand arising from unsuitable size of Y^{3+} are effective in decreasing the interaction between this cation and crown ether ligands.

These results show that the size-fit concept is unsuccessful in explaining the trivalent lanthanide ion complexation with crown ethers in an amphiprotic solvent and the conformational change of crown ether upon complexation is a prominent factor in this kind of complexation.

II: Ohyoshi and Kohata[20] have studied the complexation of lanthanide(III) cations with 18C6 in acidic medium (C_{HClO4} = 2-4 × 10^{-4}) in methanol solutions by spectrophotometric method. Izatt *et al.*[24] have also studied these complexes by calorimetric method in the same solvent. The stability constants of complexes which were obtained by Ohyoshi and Kohata[20] are generally 4-10 times more than those by Izatt *et al.*[24]. In order to know the reason of this difference, we studied complexation of La^{3+} and Ce^{3+} cations with some crown ethers at different buffer media with various concentrations of buffered constituents. The results obtained in present study and also by Ohyoshi and Kohata[20]and Izatt *et al.*[24], are given in Table-2. The variations of log K_f as a function of C_{hex}/C_{HClO4} ratio for the La-18C6 complex are shown in Fig. 4. As illustrated in this figure, the stability of La-18C6 complex depends on C_{hex}/C_{HClO4} ratio. The log K_f value increases with decreasing C_{hex}/C_{HClO4} ratio (to ward more acidic medium) and they are very close to those obtained by Ohyoshi and Kohata[20]. On the other hand as C_{hex}/C_{HClO4} ratio increases (to ward neutral medium), the value of log K_f become closer to results obtained by Izatt *et al.*[24]. Similar behaviour was observed for other complexes. It has been found that in methanol solutions, the anionic species associate to some degree with lanthanide(III) cations[37,38]. It seems that in a solution of perchloric acid in methanol, the presence of perchloric acid may fortify the complex formation. The interaction of $CH_3OH_2^+$ with the counter ion of the Ln^{3+} cations in methanol solutions, probably weaken the Ln^{3+} interactions of these cations with their counter ion and therefore, the complexes become more stable with increasing the concentration of perchloric acid in solution.

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