

PHYSICAL CHEMISTRY
OF SOLUTIONS

Complexation Process between La^{3+} Cation
and 4'-Nitrobenzo-15-Crown-5 in Some
Binary Mixed Non-Aqueous Solvents¹

S. Asgharpour, G. H. Ronaghi*, M. Mohajeri, and F. Karimian

Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran

* e-mail: ronaghi0970@mshdi.au.ac.ir; ghrounaghi@yahoo.com

Received October 23, 2014

Abstract—The complexation reaction between 4'-nitrobenzo-15-crown-5 (4'-NB15C5) with La^{3+} cation was studied in ethanol-acetonitrile (EtOH-AN), ethanol-methylacetate (EtOH-MeOAc), ethanol-1,2 dichloroethane (EtOH-DCE), and ethanol-nitrobenzene (EtOH-NB) binary mixed solvent solutions at different temperatures using the conductometric method. The results show that in most cases, the stoichiometry of the complex formed between 4'-NB15C5 and La^{3+} cation is 1 : 1 [ML]. The stability constant of (4'-nitrobenzo-15C5La)³⁺ complex changes by the nature and composition of the solvents systems. The stability order of (4'-nitrobenzo-15C5La)³⁺ complex in the binary mixed solvents with 10 mol % of ethanol at 25°C was found to be: EtOH-MeOAc > EtOH-NB > EtOH-AN ~ EtOH-DCE. A non-linear behavior was observed for variations of $\log K_f$ of the complex in terms of the solvent composition. The standard values of the thermodynamic parameters (ΔH_c° , ΔS_c°) for complexation reaction were obtained from temperature dependence of the stability constant of the complex and the results show that, in most solvent systems, the complexation reaction between La^{3+} and 4'-NB15C5 is entropy stabilized, but from enthalpy view point, except in a few cases, it is athermic.

DOI: 10.1134/S0036023615100034

INTRODUCTION

Pedersen first discovered the complexation of crown ethers with alkali metal ions [1]. The formation of complexes by binding of metal cations is caused by electrostatic ion-dipole interaction between the cations and electron-rich oxygen donor atoms present in the polyether ring. The stability of these complexes depends on the relative sizes of the cation and the cavity size of the polyether ring. The factors which influence the stability of crown ether-metal cation complexes are: the relative sizes of the crown ether cavity and the metal ion; the number of the oxygen atoms in the crown ether ring; the coplanarity structure of the crown ether ring; the symmetrical placement of the oxygen atoms; the basicity of the oxygen donor atoms; steric hindrance in the crown ether ring; the tendency of the ion to associate with the solvent [2]. The observation that macrocyclic crown ethers form stable complexes with rare earth metal cations has stimulated a great deal of interest in these compounds because of their possible applications in various branches of chemistry and biology.

Among the many different kinds of crown ether compounds, some of the most popular and fundamental types are monobenzo and dibenzo crown ethers. By introduction of various kinds of functionalities on the aromatic unit of such crown ethers through electrophilic substitution reactions, the properties of crown ethers may be altered to give improved metal ion complexation and transport ability [3, 4]. Among the recently synthesized crown ethers, the reports about the chemical behaviors of 4'-nitrobenzo-15C5 are rare and it has received a great deal of attention due to its selectivity in metal ion complexation ability.

Lanthanum was discovered in 1839 by a Swedish scientist, Carl Gustav Mosander. Lanthanum is considered biologically inactive and non-essential. Toxicological data for La, and the rare earth element (REE) in general, are relatively scarce, but the toxicity of La is generally considered to be moderate to low. Inhaled REE as a dust probably causes pneumoconiosis, and ingested REEs can accumulate in the skeleton, teeth, liver and lungs. It is the most electropositive (cationic) element of the rare earth group, is uniformly trivalent, and its binding is almost exclusively ionic. It is a hard 'acceptor' with an overwhelming preference for oxygen containing anions. Therefore,

¹ The article is published in the original.

the most common biological ligands are the carboxyl and phosphate groups with which it can form very tight complexes [5]. There are several lanthanum compounds that are available commercially. These include oxide, carbonate, chloride and fluoride. Among these compounds, lanthanum carbonate has been used in the medical industry for preparing a pharmaceutical drug. Fosrenol ($\text{La}_2(\text{CO}_3)_3$), the FDA (US Food and Drug Administration) approved drug, is used as a phosphate binding agent for patients with hyperphosphataemia. Another application of lanthanum is found to be in water treatment, for removing oxyanions, such as phosphate and arsenate.

From the soil, lanthanides are transported to lakes, rivers and ground water and consequently to the plants growing in the area, animals and humans, where their different amounts are accumulated in different tissues. It has been found that in the human organism, higher amounts of lanthanides accumulate in cancer cells than in healthy ones, which may mean that lanthanides could be used in diagnosing cancer and its treatment. Studies on eliminating of lanthanides from animal organisms has been studied using strong complexing agents such as N-phosphonomethyl glycine. The effect of lanthanides on cultivated plants and fruit trees has also been investigated. The results show that the presence of lanthanides in plant tissues increases absorption of nitrogen, phosphorus and potassium, thus accelerating the process of ripening of plants and increasing the growth of their mass; the color of the vegetables and fruit is more intense, their taste is better and their nutritive value higher. The positive effect of lanthanides on plants has given rise to increasing interest in studies on their use as a supplement to artificial fertilizers [6]. Because of the increasing interest in bioinorganic and coordination chemistry, as well as, in the increased industrial use of lanthanum compounds and their enhanced discharge, toxic properties and other adverse effects, the study of complexation process of the La^{3+} cation with the macrocyclic ligands such as crown ethers is important.

In the present work, we studied the complex formation between the La^{3+} cation and the macrocyclic ligand, 4'-NB15C5, in pure EtOH, AN, MeOAc, and DCE and also in EtOH-AN, EtOH-MeOAc, EtOH-DCE and EtOH-NB binary solvent systems at various temperatures using the conductometric method. The effects of the solvent properties on the stability, stoichiometry, and also the thermodynamics of the complexation process between La^{3+} and 4'-nitrobenzo-15C5 are discussed in this paper.

REAGENTS AND APPARATUS

The analytical-grade, 4'-NB15C5 and lanthanum(III) nitrate (with highest purity, >99%) were purchased from Merck Company and were used without any further purification except for vacuum drying. The solvents: acetonitrile, 1,2-dichloroethane, ethanol,

methylacetate and nitrobenzene, all from Merck, were used with the highest purity. The conductivity of each solvent was less than $3.0 \times 10^{-7} \text{ S}^{-1} \text{ cm}^{-1}$ at 298.15 K.

The conductance measurements were performed using a digital, WTW conductivity apparatus model LF2000 in a water bath thermostated with a constant temperature within $\pm 0.03^\circ\text{C}$. 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 0.958 cm^{-1} was used throughout the studies.

PROCEDURE

In order to study the complexation process between 4'-NB15C5 and La^{3+} , 20 mL of the metal salt solution ($5 \times 10^{-4} \text{ M}$) was placed in titration cell. The conductance of the solution was measured at each fixed temperature. Then, a known amount of the macrocycle solution prepared in the same solvent ($2 \times 10^{-2} \text{ M}$), was added in a stepwise manner using a pre-calibrated microburette. The conductances of the solutions were measured at the equilibrium temperature. This procedure was continued until the total concentration of the ligand was approximately five times higher than that of the metal cation. The conductance of the solution was measured after each addition, and the data were used for the calculation of the stability constant of the 1 : 1 [ML] complex in various solvent systems.

RESULTS AND DISCUSSION

Conductance Studies

The changes of the molar conductivity (Λ_m) versus the ligand to cation molar ratio ($[\text{L}]_t/[\text{M}]_t$) for complexation of 4'-nitrobenzo-15C5 with La^{3+} cation was measured in pure AN, EtOH, DCE and MeOAc, and also in their binary solvent solutions at various temperatures. $[\text{L}]_t$ is the total concentration of the ligand and $[\text{M}]_t$ is the total concentration of the metal cation. Two typical examples of molar conductance–mole ratio plots for the complex which was formed between 4'-nitrobenzo-15C5 and La^{3+} cation in two different solvent systems at various temperatures are shown in Figs. 1 and 2.

Investigation of the molar conductivity plots for formation of $(4'\text{-nitrobenzo-15C5La})^{3+}$ complex shows that the slope of molar conductivity curves at different temperatures changes sharply up to the point that the ligand to cation mole ratio is about 1 which is an evidence for formation of a 1 : 1 [M : L] complex between the La^{3+} cation and the macrocyclic ligand. In order to make more clear the 1 : 1 [M : L] complexation model, the fitting and experimental curves for $(4'\text{-nitrobenzo-15C5La})^{3+}$ complex in EtOH-DCE (mol % EtOH = 25%) at 298.15 K is shown in Fig. 3. As is evident in this figure, there is a very good agreement between the fitting and experimental data.

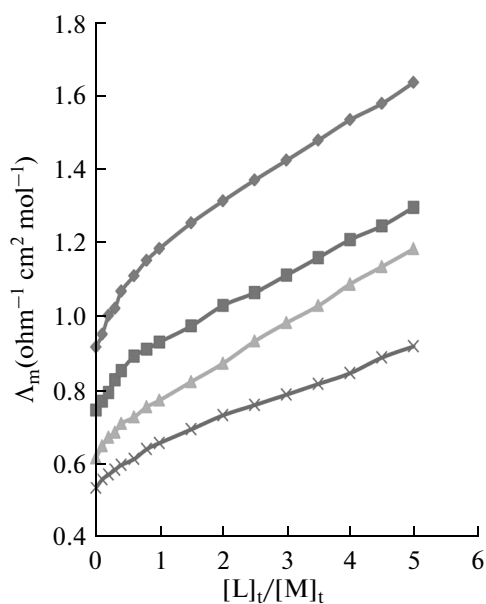


Fig. 1. Molar conductance–mole ratio plots for (4'-nitrobenzo-15C5La)³⁺ complex in pure EtOH, at different temperatures: (x) 45°C, (▲) 35°C, (■) 25°C, (◆) 15°C.

As is evident from Figs. 1 and 2, addition of 4'-NB15C5 to La³⁺ cation solution in pure EtOH and EtOH-NB (mol % NB = 90%) binary solvent system, results an increase in molar conductivity, which indicates that the (4'-nitrobenzo-15C5La)³⁺ complex in these solvent systems is more mobile than free solvated

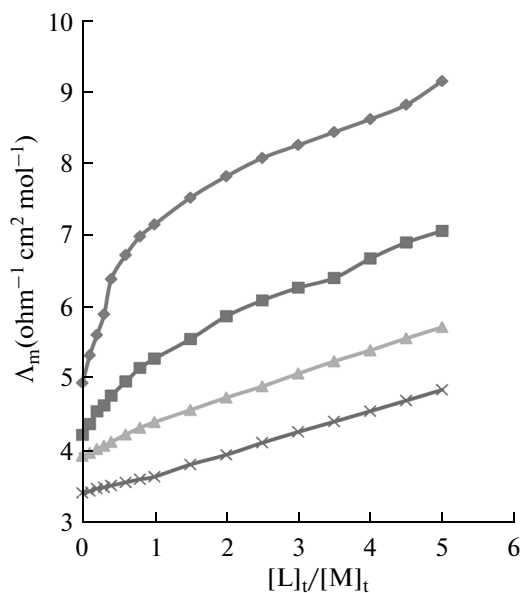


Fig. 2. Molar conductance–mole ratio plots for (4'-nitrobenzo-15C5La)³⁺ complex in EtOH-NB binary system (mol % NB = 90%), at different temperatures: (x) 45°C, (▲) 35°C, (■) 25°C, (◆) 15°C.

La³⁺ cation. Somewhat similar behavior was observed in the other solvent systems. Since the (4'-nitrobenzo-15C5La)³⁺ complex is more bulky than La³⁺ cation, therefore, it is much less solvated by the solvent molecules, and hence its mobility increases with respect to the free solvated La³⁺ cation. It is obvious from these Figures, that as the temperature increases, the curvature of the molar conductivity plots of (4'-nitrobenzo-15C5La)³⁺ complex decreases which is an evidence for formation of a weaker complex at higher temperatures. Therefore, the complexation process between 4'-NB15C5 and La³⁺ cation is exothermic.

Stability Constant of the Metal Ion-Ligand System

The stability constant of (4'-nitrobenzo-15C5La)³⁺ complex at each temperature was calculated from the changes of the molar conductance as a function of [4'-nitrobenzo-15C5]/[La³⁺] molar ratios using a GENPLOT computer program [7]. The details of calculation of the stability constants of complexes by conductometric method have been described in reference [8]. The obtained values of the stability constant ($\log K_f$) for (4'-nitrobenzo-15C5La)³⁺ complex in various solvent systems are listed in Table 1. As is evident from this Table, the stability order of (4'-nitrobenzo-15C5La)³⁺ complex in the studied binary solvent systems at 25°C with 10 mole percent of EtOH was found to be: EtOH-MeOAc > EtOH-NB > EtOH-AN ~ EtOH-DCE. But at 15°C at the same composition it changes to: EtOH-NB > EtOH-MeOAc > EtOH-AN ~ EtOH-DCE. The results obtained in the present work, show that the stability order of the (4'-nitrobenzo-15C5La)³⁺ complex changes with the composition of the binary solvent solutions as well as with the temperature.

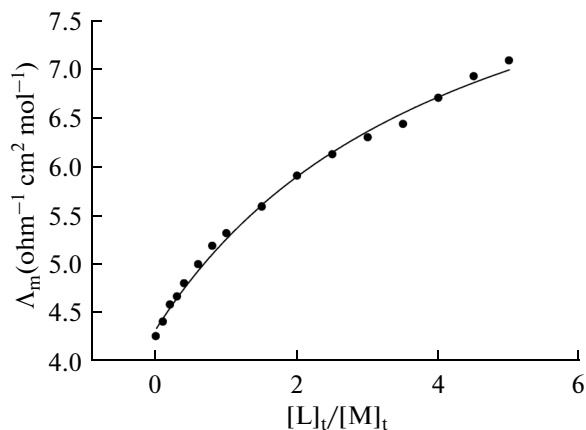


Fig. 3. The fitting and experimental curves for (4'-nitrobenzo-15C5La)³⁺ complex in EtOH-NB (mol % NB = 90%) binary solvent system at 298.15 K.

Table 1. Stability constant ($\log K_f$) values for the (4'-nitrobenzo-15C5La)³⁺ complex in EtOH-AN, EtOH-MeOAc, EtOH-DCE and EtOH-NB binary mixtures

Medium	Mol % EtOH	$\log K_f \pm SD^a$			
		288.15 K	298.15 K	308.15 K	318.15 K
EtOH-AN	100	3.22 ± 0.16	2.72 ± 0.11	2.59 ± 0.12	2.68 ± 0.12
	75	2.58 ± 0.12	2.69 ± 0.13	2.71 ± 0.13	2.61 ± 0.30
	50	2.70 ± 0.12	2.71 ± 0.11	2.71 ± 0.11	2.69 ± 0.12
	25	2.75 ± 0.12	2.67 ± 0.13	2.73 ± 0.10	2.57 ± 0.13
	10	2.85 ± 0.14	2.70 ± 0.12	2.57 ± 0.15	2.79 ± 0.10
EtOH-MeOAc	100	3.22 ± 0.16	2.72 ± 0.11	2.59 ± 0.12	2.68 ± 0.12
	75	2.68 ± 0.12	2.69 ± 0.12	2.68 ± 0.12	2.73 ± 0.09
	50	2.72 ± 0.11	2.74 ± 0.10	2.62 ± 0.17	2.70 ± 0.12
	25	2.79 ± 0.09	2.81 ± 0.12	2.89 ± 0.16	2.81 ± 13
	10	3.41 ± 0.10	3.71 ± 0.14	2.52 ± 0.30	2.93 ± 0.16
EtOH-DCE	100	3.22 ± 0.16	2.72 ± 0.11	2.59 ± 0.12	2.68 ± 0.12
	75	2.70 ± 0.11	2.70 ± 0.11	2.71 ± 0.10	2.68 ± 0.13
	50	2.76 ± 0.09	2.58 ± 0.12	2.75 ± 0.13	2.57 ± 0.14
	25	2.79 ± 0.08	2.69 ± 0.11	2.57 ± 0.13	2.68 ± 0.11
	10	2.72 ± 0.17	2.79 ± 0.10	2.70 ± 0.15	2.55 ± 0.17
EtOH-NB	100	3.22 ± 0.16	2.72 ± 0.11	2.59 ± 0.12	2.68 ± 0.12
	75	2.78 ± 0.13	2.73 ± 0.10	2.71 ± 0.11	2.92 ± 0.10
	50	2.82 ± 0.15	2.71 ± 0.11	2.69 ± 0.11	2.59 ± 0.11
	25	3.94 ± 0.18	3.10 ± 0.08	3.37 ± 0.10	2.57 ± 0.16
	10	4.18 ± 0.13	3.48 ± 0.08	2.74 ± 0.08	2.51 ± 0.20

^aSD = standard deviation.*Effect of Solvent upon the Complexation Reaction*

The solvation process plays a major role in molecular and cationic recognition influencing the stability of molecular conformation. The structure and conformation of such molecules are essential to rule out their ionophoric properties, however, the complex formation and ion transport phenomena in solution are still not completely understood. The data given in Table 1, clearly illustrate the fundamental role of the solvent properties upon complex formation between the La³⁺ cation and 4'-NB15C5. Comparison of the data given in this table, reveals that, the (4'-nitrobenzo-15C5La)³⁺ complex is more stable in the EtOH-MeOAc binary mixed systems compared with other binary mixed solvent solutions. This can be attributed to the lower dielectric constant of MeOAc ($\epsilon = 6.7$) compared with DCE ($\epsilon = 10.4$), NB ($\epsilon = 34.82$) and AN ($\epsilon = 36$), therefore, an increase in electrostatic interaction between 4.-NB15C5 and the La³⁺ cation in solution. Consideration of $\log K_f$ for (4'-nitrobenzo-

15C5La)³⁺ complex, with the mole ratio of 10% with respect to EtOH, shows that the stability constant of (4'-nitrobenzo-15C5La)³⁺ in the binary mixed solvents at 25°C is: EtOH-MeOAc > EtOH-NB > EtOH-AN ~ EtOH-DCE. This indicates that the dielectric constant of the solvent is not a dominant factor in this complexation reaction. Unexpected behavior of DCE may be related to changes occurring in the structure of the solvent mixtures and, therefore, to changes in the solvation properties of the cyclic polyether, cation and even the resulting complex, in these solvent mixtures. These structural changes may result in changing of the interactions of these solvents with the solutes.

In addition, preferential solvation of the cation, anion and ligand, and their changes with the composition of the mixed solvents and temperature may affect the complexation processes. 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

Table 2. Thermodynamic parameters for the (4'-nitrobenzo-15C5La)³⁺ complex in EtOH-AN, EtOH-MeOAc, EtOH-DCE and EtOH-NB binary mixtures

Medium	Mol % EtOH	$-\Delta G_c^\circ \pm \text{SD}^a$ (at 25°C)	$\Delta H_c^\circ \pm \text{SD}^a$	$\Delta S_c^\circ \pm \text{SD}^a$
		(kJ mol ⁻¹)	(kJ mol ⁻¹)	(J mol ⁻¹ K ⁻¹)
EtOH-AN	100	15.51 ± 0.64	0	0
	75	15.34 ± 0.76	0	58.41 ± 9.33
	50	15.51 ± 0.65	0	49.22 ± 3.50
	25	15.26 ± 0.76	0	53.68 ± 11.35
	10	15.43 ± 0.71	0	0
EtOH-MeOAc	100	15.51 ± 0.64	0	0
	75	15.36 ± 0.66	0	59.91 ± 4.80
	50	15.63 ± 0.59	0	40.70 ± 14.00
	25	16.06 ± 0.69	0	62.85 ± 13.00
	10	18.09 ± 0.84	0	0
EtOH-DCE	100	15.51 ± 0.64	0	0
	75	15.40 ± 0.63	0	49.33 ± 3.00
	50	14.73 ± 0.74	0	0
	25	15.38 ± 0.66	0	0
	10	15.95 ± 0.58	0	0
EtOH-NB	100	15.51 ± 0.64	0	0
	75	15.60 ± 0.61	0	72.992 ± 5.00
	50	15.44 ± 0.66	-12.47 ± -2.40	0
	25	17.67 ± 0.50	-66.90 ± 26.82	0
	10	19.84 ± 0.46	-100.27 ± 12.20	-269.75 ± 40.00

^aSD = standard deviation.

the ion and the interactions between the 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 [31].

Standard Thermodynamic Parameters for the Complexation Process

The van't Hoff plots of $\ln K_f$ versus $1/T$ for all of the investigated solvent systems were constructed. The changes in the standard enthalpy (ΔH_c°) for the com-

plexation reaction were obtained from the slope of the van't Hoff plots assuming that ΔC_p is equal to zero over the entire temperature range investigated. The changes in the standard entropy (ΔS_c°) were calculated from the relationship $\Delta G_{c,298.15}^\circ = \Delta H_c^\circ - 298.15\Delta S_c^\circ$. The thermodynamic data are summarized in Table 2. As is evident from this Table, in most cases, the complexation reaction between 4'-NB15C5 and the La³⁺ cation in the binary solvent solutions is entropy stabilized. The experimental results which are given in Table 1, indicate that in the most solvent systems, the stability of the (4'-nitrobenzo-15C5La)³⁺ complex does not change within experimental error

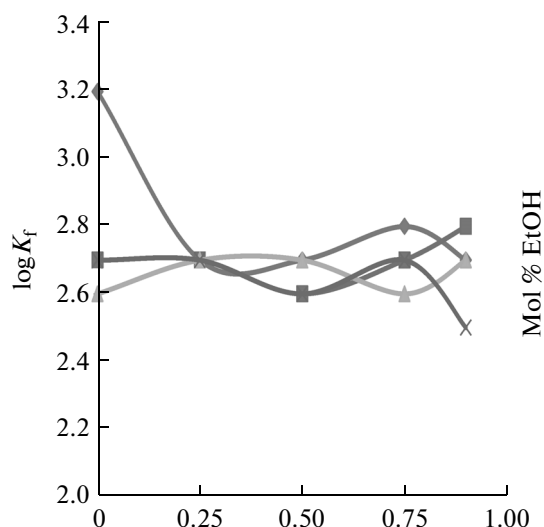


Fig. 4. Changes of formation constant of $(4'\text{-nitrobenzo-15C5La})^{3+}$ complex with the composition of EtOH-DCE binary system at different temperature: (x) 45°C , (\blacktriangle) 35°C , (\blacksquare) 25°C , (\blacklozenge) 15°C .

with temperature and the slope of the van't Hoff plots is nearly zero which show that the complexation process between 4'-NB15C5 and La^{3+} is athermic in these binary solvent solutions.

As seen from Fig. 4, the change of the stability constant ($\log K_f$) of $(4'\text{-nitrobenzo-15C5La})^{3+}$ complex versus the composition of EtOH-DCE binary solvent solution changes non-monotonically with the composition of the mixed solvents. Somewhat similar behavior was observed in the other binary mixed solvent systems. This anomalous behavior may be related to changes occurring in the structure of the solvent mixtures due to the interactions between these dipolar organic solvents and, therefore, changing the solvation number of the dissolved species in the solution. In addition, the heteroselective solvation of the metal cation, ligand and even the resulting complex and formation of the mixed solvates, may be effective in such a behavior.

CONCLUSIONS

The results obtained for complexation of La^{3+} cation with 4'-NB15C5 in methanol, acetonitrile, meth-

ylacetate, dichloroethane and their binary solvent systems show that the stability and thermodynamics of complexation reaction between La^{3+} cation and macrocyclic ligand, 4'-NB15C5 is governed by the nature and composition of the solvent medium. 4'-NB15C5 forms a 1 : 1 complex with La^{3+} cation in all solvent systems. The changes in the stability constant ($\log K_f$) of the complex versus the composition of the mixed solvents are non-linear. This behavior is probably due to a change in the structure of the binary solvent solutions as their composition is varied. The results obtained in the present work, show that the stability order of the $(4'\text{-nitrobenzo-15C5La})^{3+}$ complex changes with the composition of the binary solvent solutions as well as with the temperature. Therefore, results indicate the possibility of changes in stabilities of metal ion-macrocyclic complexes and, therefore, changes of selectivities of the ligands which may be obtained in certain composition of the mixed solvent systems. The experimental results show that in most studied solvent systems, the complexation process is athermic, but in a few cases it is exothermic. In addition, in most solvents the $(4'\text{-nitrobenzo-15C5La})^{3+}$ complex is stabilized from entropy view point.

ACKNOWLEDGMENTS

We gratefully acknowledge the support of this work by Islamic Azad University, Mashhad Branch, Iran.

REFERENCES

1. C. J. Pedersen, *J. Am. Chem. Soc.* **89**, 2495 (1967).
2. C. J. Pedersen, *J. Am. Chem. Soc.* **89**, 7017 (1967).
3. R. M. Izatt, K. Pawlak, J. S. Bradshaw, and R.L. Bruening, *Chem. Rev.* **91**, 1721 (1991).
4. J. C. Lee, *Synthesis of Novel Crown Ether Compounds and Ionomer Modification of Nafion*, PhD Dissertation, 1992.
5. G. J. Persy, A. R. Behets, Bervoets, et al., *Sem. Dialysis* **19**, 195 (2006).
6. W. Brzyska, *Lantanowce i aktynowce* (WNT, Warszawa, 1996).
7. GENPLOT, Computer Graphic Service, USA (1989).
8. G. H. Rounaghi, Eshaghi, and E. Ghiamati, *Talanta*, **44**, 275 (1997).