Thermodynamic Study of Complex Formation Between Benzo-15-crown-5 and Phenylaza-15-crown-5 with La³⁺ Cation

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The equilibrium constants and the thermodynamic parameters for complex formation of benzo-15-crown-5 (B15C5) and phenylaza-15-crown-5 (PhA15C5) with La³⁺ cation have been determined by conductivity measurements in acetonitrile-dimethylformamide (AN/DMF), acetonitrile-dimethyl sulfoxide (AN/DMSO), acetonitrile-1,2-dichloroethane (AN/1,2DCE) and acetonitrile-chloroform (AN/CHCl₃) binary solutions. Phenylaza-15-crown-5 forms a 1:1 complex [M:L] with La³⁺ cation, but in the case of benzo-15-crown-5 ligand, a 1:2 [M:L₂] complex is formed in some binary solutions. The stability of the complexes is sensitive to the solvent composition and a non-linear behaviour was observed for variation of log K_f of the 1:1 complexes *versus* the composition of the binary mixed solvents. The thermodynamic parameters ($\Delta H°_c$, $\Delta S°_c$) for formation of (B15C5.La)³⁺ and (PhA15C5.La)³⁺ complexes were obtained from temperature dependence of the stability constant using the Van't Hoff plots. The results show that in most of the cases, the complexes are both enthalpy and entropy stabilized. A non-linear behaviour was observed for changes of log K_f of the 1:1 complexes *versus* the composition of the binary mixed solvents which was explained in terms of solvent-solvent interactions and also the heteroselective solvation of the species involved in the complexation reactions.

Key Words: Benzo-15-crown-5, Phenylaza-15-crown-5, La³⁺ cation, Mixed non-aqueous solvents, Conductometry.

INTRODUCTION

Crown ethers are macrocyclic polyethers which form stable selective complexes with suitable cations. The important characteristics of crown ethers are the number and type of donor atoms present in polyether ring, the dimension of the macrocycle cavity and the preorganization of the host molecule for most effective coordination. The so-called, macrocyclic effect, of crown ethers is related to the last two characteristics.

The ability of crown ethers to form stable complexes with cations has spurred interest in these compounds[1]. These compounds have aroused a great interest in recent years because of their characteristics which are of importance in preparation chemistry and in biology.

Considerable researches have been carried out on a wide range of applications of these macrocyclic compounds in different areas such as designing of sensors[2], as stationary phase in chromatography columns[3-6], recognition of isomers[7], construction of ion-selective electrodes[8-11], separation of metal ions[12] and chemical analysis[13]. Most of applications of crown compounds are based on their complexing ability with various cations.

Various investigations have extensively studied thermodynamics of solution of macrocyclic polyether complexes during the past three decades[14-19] and Izatt and coworkers have compiled kinetic data[20]. Although the complexation process between large macrocyclic crown ethers and metal cations has been extensively studied in solutions, but the complexation of metal cations by small crown ethers such as benzo-15-crown-5 has been studied to a limited extent especially in non-aqueous solvents and their binary solutions. Trivalent lanthanides are expected to form stable complexes with various macrocyclic ligands similarly to alkali and alkaline earth metals because of the similarity of the radii between lanthanides and Na⁺ or Ca²⁺ ions. However, attention has been focused, mainly on the complexes of alkali and alkaline earth metal ions. Several studies have been carried out to enhance the selectivity in the separation of lanthanides and actinides elements in the extraction systems based on the size-fitting effect of the crown ethers[21-25]. Lanthanum salts are generally considered to have low or moderate toxicity. Lanthanum nitrate treatment promotes germination of neutral rice seed[26]. Because of the increasing industrial use of lanthanum compounds as well as their enhanced discharge and its useful and harmful biological activity, the study of complex formation of lanthanum with crown ethers has been of a recent increasing concern[27].

One of our main research interests is the influence of solvent properties on the thermodynamics of complexation

reactions of macrocyclic ligands with lanthanum. In the present paper, we report the results which are obtained from conductometric study of the complexation reaction of La³⁺ cation with macrocyclic ligand, benzo-15-crown-5 and phenylaza-15-crown-5 in acetonitrile-dimethyl formamide (AN/DMF), acetonitrile-dimethyl solfoxide (AN/DMSO), acetonitrile-1,2-dichloroethane (AN/1,2DCE) and acetonitrile-chloroform (AN/CHCl₃) binary solutions at different temperatures.

EXPERIMENTAL

Benzo-15-crown-5 (Fluka), phenylaza-15-crown-5 (Fluka) and La(NO₃)₃·6H₂O (Merck) were used without further purification. The solvents *i.e.*, acetonitrile, dimethyl formamide, dimethyl sulfoxide, chloroform and 1,2-dichloroethane all from Merck company were used with the highest purity. The experimental procedure to obtain the stability constants of complexes is as follows: a solution of lanthanum salt (1.0 × 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 crown ether solution prepared in the same solvent (2.0 × 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.

The conductance measurements were performed on a digital AMEL conductivity apparatus, model 160, in a water bath thermostated at a constant temperature which maintained within ± 0.03 °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 0.73 cm⁻¹ was used throughout the studies.

RESULTS AND DISCUSSION

The changes of molar conductivity (Λ_m) *versus* the ligand to the cation molar ratio ([La³⁺]/[B15C5]) and ([La³⁺]/[PhA15C5]), for complexation of B15C5 and PhA15C5 with La³⁺ cation was measured in pure AN and DMF and also in AN-DMF, AN-DMSO, AN-1,2DCE and AN-CHCl₃ binary systems at different temperatures.

The changes of Λ_m *versus* ligand/cation mole ratio ([L]ₜ/[M]ₜ) for (B15C5.La)³⁺ complex in a binary mixture of AN-1,2DCE (mol % AN = 75) and for (PhA15C5.La)³⁺ and (B15C5.La)³⁺ complexes in AN-CHCl₃ (mol % AN = 75) binary solutions are shown in Figs. 1-3, respectively.

The stability constant of the complexes at each temperature was obtained from variation of molar conductance as a function of [L]ₜ/[M]ₜ molar ratio plots using a GENPLOT computer program[28]. The details of calculation of the stability constants of complexes by conductometric method have been described in reference[29]. The values of the stability constant (log Kf) for the (PhA15C5.La)³⁺ and (B15C5.La)³⁺ complexes in various solvent systems are listed in Tables 1 and 2, respectively. The van't Hoff plots of ln Kf *versus* 1/T for all of the investigated systems were constructed. A typical example of these plots is shown in Fig. 4. The changes in standard enthalpy ($\Delta H°_c$) for complexation reactions 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 standard entropy ($\Delta S°_c$) were calculated from the
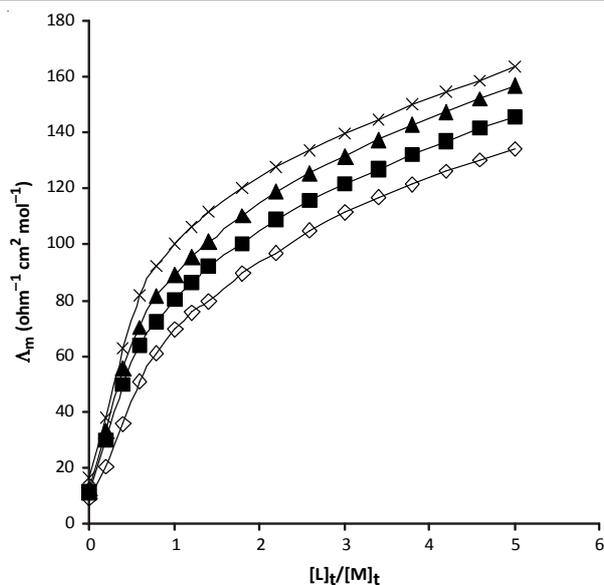
Fig. 1. Molar conductance-mole ratio plots for (B15C5.La)³⁺ complex in AN/1,2DCE (mol % AN = 75) at different temperatures (◇ = 20 °C, ■ = 30 °C, ▲ = 40 °C , × = 50 °C)
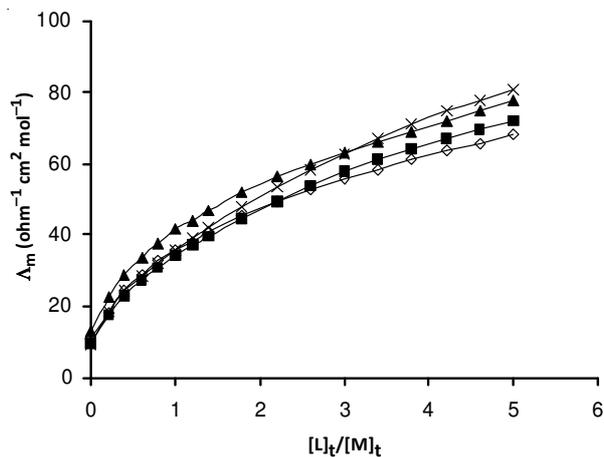
Fig. 2. Molar conductance-mole ratio plots for (PhA15C5.La)³⁺ complex in AN/CHCl₃ (mol % AN = 75) at different temperatures (◇ = 20 °C, ■ = 30 °C, ▲ = 40 °C , × = 50 °C)
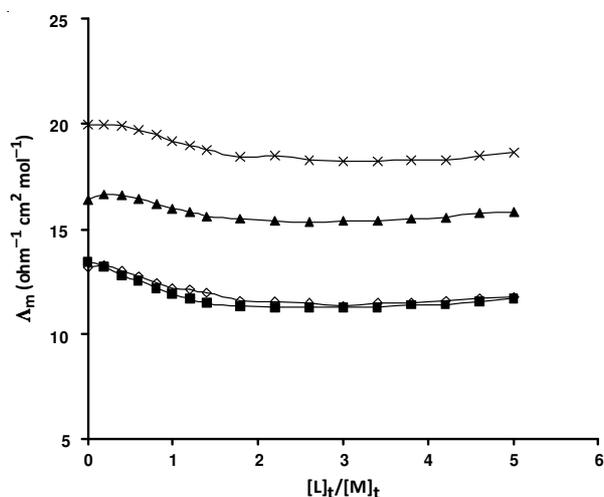
Fig. 3. Molar conductance-mole ratio plots for (B15C5.La)³⁺ complex in AN/CHCl₃ (mol % AN = 75) at different temperatures (◇ = 20 ºC, ■ = 30 °C, ▲ = 40 °C , × = 50 °C)

TABLE-1
log K_f VALUES OF (PhA15C5.La)$^{3+}$ COMPLEX IN AN-DMF, AN-DMSO, AN-1,2DCE AND AN-CHCl$_3$ BINARY MIXTURES AT DIFFERENT TEMPERATURES (ºC)

Medium mol % AN	log K_f (±SD)[a]			
	20 ºC	30 ºC	40 ºC	50 ºC
AN-DMF[b]				
100	3.20±0.06	3.02±0.04	3.19±0.04	3.00±0.20
75	3.34±0.04	3.36±0.03	3.28±0.04	2.93±0.06
50	3.22±0.05	3.13±0.06	3.16±0.05	3.14±0.05
25	3.24±0.04	3.16±0.05	2.97±0.04	3.12±0.09
0	3.36±0.03	3.21±0.06	3.24±0.05	3.14±0.05
AN-DMSO[b]				
100	3.20±0.06	3.02±0.04	3.19±0.04	3.02±0.20
75	3.32±0.04	2.97±0.06	3.12±0.05	2.71±0.06
50	3.2±0.05	3.30±0.07	2.91±0.03	2.78±0.05
25	3.14±0.06	3.05±0.06	2.69±0.06	2.68±0.07
0	c	c	c	c
AN-1,2DCE[b]				
100	3.20±0.06	3.02±0.04	3.19±0.04	3.02±0.20
75	3.96±0.05	4.05±0.07	4.12±0.08	4.27±0.09
50	c	c	c	c
AN-CHCl$_3$[b]				
100	3.20±0.06	3.02±0.04	3.19±0.04	3.02±0.20
75	3.75±0.05	3.58±0.05	3.8±0.06	3.43±0.06
50	c	c	c	c

[a]Standard deviation; [b]The composition of solvent systems is expressed in mol % of each solvent; [c]The salt are not dissolved in these solvent systems.

TABLE-2
log K_f VALUES OF (B15C5.La)$^{3+}$ COMPLEX IN AN-DMF, AN-DMSO, AN-1,2DCE AND AN-CHCl$_3$ BINARY MIXTURES AT DIFFERENT TEMPERATURES (ºC)

Medium mol % AN	log K_f (±SD)[a]			
	20 ºC	30 ºC	40 ºC	50 ºC
AN-DMF[b]				
100	c	3.07±0.07	3.40±0.08	c
75	3.34±0.04	3.27±0.04	3.20±0.04	2.71±0.06
50	3.08±0.06	3.39±0.04	2.94±0.06	2.67±0.05
25	3.38±0.04	3.32±0.03	3.32±0.04	2.95±0.06
0	2.7±0.1	3.20±0.05	3.34±0.03	2.91±0.06
AN-DMSO[b]				
100	c	3.07±0.07	3.40±0.08	c
75	3.27±0.04	3.19±0.05	3.13±0.05	3.15±0.05
50	3.35±0.04	3.34±0.05	3.09±0.07	3.16±0.04
25	3.15±0.08	3.1±0.05	3.45±0.07	2.92±0.07
0	d	d	d	d
AN-1,2DCE[b]				
100	c	3.07±0.07	3.40±0.08	c
75	c	c	c	c
50	d	d	d	d
AN-CHCl$_3$[b]				
100	c	3.07±0.07	3.40±0.08	c
75	c	c	c	c
50	d	d	d	d

[a]Standard deviation; [b]The composition of solvent systems is expressed in mol % of each solvent; [c]The data can not be fitted in equation; [d]The salt are not dissolved in these solvent systems.

relationship $\Delta G°_{c,293.15} = \Delta H°_c - 293.15\Delta S°_c$. The results are summarized in Tables 3 and 4. The changes of log K_f of (B15C5.La)$^{3+}$ complex *versus* the mole fraction of AN in AN-DMSO binary systems at different temperatures are shown in Fig. 5.
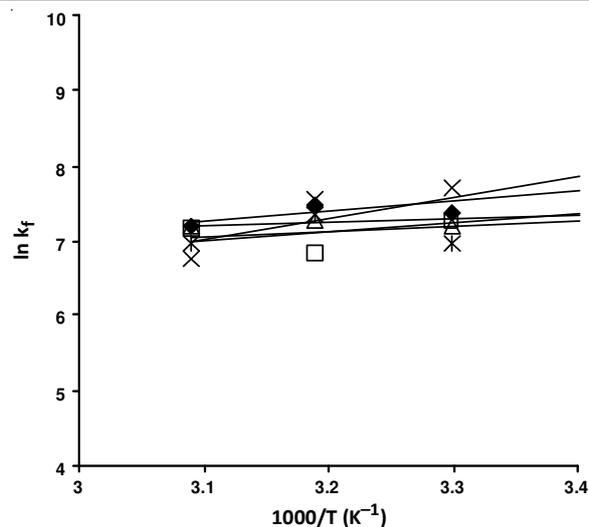
Fig. 4.   Van't Hoff plots for (PhA15C5.La)$^{3+}$ in AN-DMF binary systems (mol % AN: ◆ = 0, □ = 25, × = 50, ▲ = 75, * = 100)

TABLE-3
THERMODYNAMIC PARAMETERS FOR (PhA15C5.La)$^{3+}$ COMPLEX IN AN-DMF, AN-DMSO, AN-1,2DCE AND AN-CHCl$_3$ BINARY MIXTURES

Medium mol % AN	$-\Delta G°_c$ (KJ mol^{-1})	$-\Delta H°_c$ (J mol^{-1})	$-\Delta S°_c$ (J mol^{-1} K^{-1})
AN-DMF[b]			
100	18.0±0.3	a	61.0±1.0
75	18.7±0.2	2.1±1	63.9±0.7
50	18.1±0.3	a	62.0±1.0
25	18.2±0.2	a	62.0±0.8
0	18.9±0.2	5±2	64.3±0.6
AN-DMSO[b]			
100	18.0±0.3	a	61.0±1.0
75	18.3±0.2	a	62.5±0.8
50	18.8±0.2	a	64.2±0.8
25	17.6±0.4	2.0±0.5	60.0±1.0
AN-1,2DCE[b]			
100	18.0±0.3	a	61.0±1.0
75	22.2±0.3	3.7±0.5	76.0±1.0
AN-CHCl$_3$[b]			
100	18.0±0.3	a	61±1
75	21.0±0.3	a	72±1

[a]The data are estimated with high uncertainties; [b]The composition of solvent systems is expressed in mol% of each solvent.

TABLE-4
THERMODYNAMIC PARAMETERS FOR (B15C5.La)$^{3+}$ COMPLEX IN AN-DMF AND AN-DMSO BINARY MIXTURES

Medium mol % AN	$-\Delta G°_c$ (KJ mol^{-1})	$-\Delta H°_c$ (J mol^{-1})	$-\Delta S°_c$ (J mol^{-1} K^{-1})
AN-DMF[b]			
100	c	c	c
75	18.7±0.2	1.5±0.6	63.9±0.8
50	17.3±0.3	1.2±0.8	59.0±1.0
25	19.0±0.2	a	64.7±0.7
0	15.3±0.6	a	52.0±2.0
AN-DMSO[b]			
100	c	c	c
75	18.3±0.2	7±3	62.5±0.8
50	18.8±0.2	a	64.2±0.8
25	17.7±0.5	a	60.0±4.0

[a]The data are estimated with high uncertainties; [b]The composition of solvent systems is expressed in mol% of each solvent; [c]The salt are not dissolved in these solvent systems.
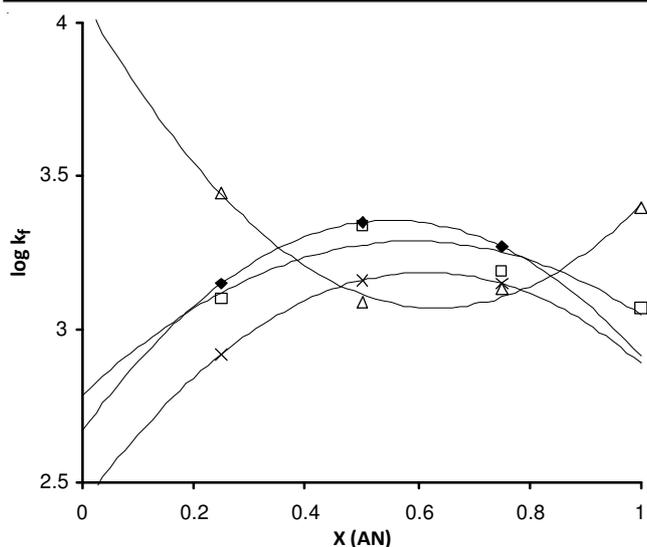
Fig. 5. Changes of stability constant (log K_f) of (B15C5.La)³⁺ complex with composition of the AN-DMSO binary systems at different temperature (◆ = 20 ℃, ☐ = 30 ℃, △ = 40 ℃ , × = 50 ℃)

As is obvious from Figs. 1 and 2, addition of B15C5 ligand in AN-1,2DCE (mol % AN = 75) and PhA15C5 ligand in AN-CHCl₃ (mol % AN = 75) and AN-CHCl₃ (mol % AN = 75) binary solutions to La³⁺ solution at different temperatures, shows an increase in molar conductivity with an increase in ligand concentration. This indicates that the (B15C5.La)³⁺ and (PhA15C5.La)³⁺ complexes are more mobile than free solvated La³⁺ cation in these binary mixtures. Similar behaviour was observed for complexation of La³⁺ cation in all solvent systems except in the case of (B15C5.La)³⁺ complex in AN-CHCl₃ (mol % AN = 75) binary solution. It is evident from Figs. 1 and 2 that the slope of the corresponding molar conductivity *versus* [B15C5]/[La]³⁺ and [PhA15C5]/[La]³⁺ cation mole ratio changes at the point where the ligand to cation mole ratio is about 1, which is an evidence for formation of a relatively stable 1:1 complex between phenylaza-15-crown-5 and La³⁺ in these solvent system.

The addition of B15C5 to La³⁺ cation in AN-CHCl₃ (mol % AN = 75) at different temperatures shows a decrease in molar conductivity with an increase in the ligand concentration (Fig. 3), which indicates that the (B15C5.La)³⁺ complex in this solution is less mobile than free solvated La³⁺ cation. As evident from Fig. 3, the slope of molar conductance mole ratio plots changes at the point where [L]ₜ/[M]ₜ is about 2, which indicates the formation of a 1:2 (ML₂) complex between La³⁺ cation and B15C5 in this solution. The results obtained in this investigation show that the stoichiometry of the crown ether-metal cation complexes may be changed by the nature of the solvent systems.

The results summarized in Tables 3 and 4, show that in all cases, the values $\Delta S°_c$ for the complexation reactions between B15C5 and PhA15C5 with La³⁺ cation in binary solutions are positive, therefore, the complexation reactions are entropy stabilized. Since during the complexation of the cation by a macrocyclic ligand, most of the coordinated solvent molecules are replaced by the donor atoms of the ligand, even when the cation-macrocycle binding is weak, the increased degree of freedom, because of the desolvation of cation, may

result in positive entropic gain. In the cases where the macrocycle has also some interaction with solvent molecules, the release of some solvent molecules involved in interaction with the ligand, may also contribute to the positive entropy values[30]. It should be mentioned, however, that the complexation process involves not only a change in solvation of the cation and also that of the ligand and the change in the flexibility of the ligand upon complexation, in addition, the solvent-solvent interactions contribute to changes in entropy. The experimental values of $\Delta S°_c$ show that, the values of standard enthalpy ($\Delta S°_c$) for complexation reaction between B15C5 and PhA15C5 with La³⁺ cation in these solutions, do not vary monotonically with the solvent composition. This behaviour may be due to strong interactions between the constituent solvent molecules which result in changing in some of the chemical and physical properties of each of the solvents and therefore, changing their solvating ability towards the dissolved species. In addition, the heteroselective solvation of the cation and even the macrocyclic ligand and the character of its changes with the composition of the mixed solvent and temperature may be effective in the complexation reactions.

As is obvious from Fig. 5, the change in the stability constant (log K_f) of (B15C5.La)³⁺ complex *versus* the composition of these binary systems at various temperatures is not monotonic. Similar behaviour was observed in other binary solutions. This behaviour may be related to changes occurring in the structure of the solvent mixtures and, therefore, changing in the solvation properties of the cyclic polyether, cation and even the resulting complex in these solvent mixtures. Some structural changes probably occur in the structure of the solvents when they mix with one another. These structural changes may result in changing the interactions of those solvents with the solutes. In addition, the preferential solvation of the cation, anion and ligand and the characteristics of its changes with the composition of the mixed solvents and temperature may be effective in this complexation process. 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 the ion and the interactions between 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].

Comparison of the data given in Tables 1 and 2 reveals that, the stability of (PhA15C5.La)³⁺ and (B15C5.La)³⁺ complexes in various non-aqueous solvents decreases in the order: AN-1,2DCE > AN-CHCl₃ > AN-DMF > AN-DMSO, which is consistent with the inverse order of their solvating abilities as expressed by the Gutmann donor number.

Solvent properties are considered as the major factors influencing the formation constants of crown ether-cation complexes. The reason is that the solvent and crown ether molecules compete in binding to metal cation. When the donor properties of the solvent are low, the cation is poorly solvated and can easily be complexed by the crown ether molecule. The solvation of the crown ether may also influence the formation constant of crown-cation complex in solution.

In solvents with a high solvating ability (high donor number), such as DMSO (donor number = 29.8), AN (donor number = 14.1) and DMF (donor number = 26), the complex formation tends to be weak, since the solvent solvates the cation strongly and competes with the ligand for the cation, but in solvents with lower donicity such as 1,2DCE and $CHCl_3$, the relatively poorer solvating ability of these solvents leads to an increase in the stability constant, therefore, there is actually an inverse relationship between the stability of the complex and the solvating ability of these organic solvents.

Conclusion

The results obtained for complexation of La^{3+} cation with benzo-15-crown-5 and phenylaza-15-crown-5 in AN/DMF, AN/DMSO, AN/1,2DCE and AN/$CHCl_3$ binary mixtures show that the stability and thermodynamics of complexation are governed by the solvent medium. The conductance data show that B15C5 and PhA15C5 form 1:1 complexes with La^{3+} cation, but in the case of B15C5 ligand, a 1:2 $[ML_2]$ complex is formed in AN-$CHCl_3$ (mol % AN = 75) binary solution. Comparison of the stability constants reveals that, the stability of $(PhA15C5.La)^{3+}$ and $(B15C5.La)^{3+}$ complexes in various non-aqueous solvents decreases in the order: AN-1,2DCE > AN-$CHCl_3$ > AN-DMF > AN-DMSO, which is consistent with the inverse order of their solvating abilities as expressed by the Gutmann donor number. Therefore, the electron donor ability of the solvent plays an important role in complexation process. The changes in the stability constants (log K_f) of the complexes *versus* the composition of the mixed solvents are non-linear. In addition, a non-linear behaviour is observed between the ΔS°_c and the composition of the mixed solvents. These behaviours are probably due to a change in the structure of the binary solvents as the composition of the medium changed.

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