

# Effect of Non-Aqueous Solvents on Stoichiometry and Selectivity of Complexes Formed Between 4'-Nitrobenzo-15-Crown-5 with $\text{Fe}^{3+}$ , $\text{Y}^{3+}$ , $\text{Cd}^{2+}$ , $\text{Sn}^{4+}$ , $\text{Ce}^{3+}$ and $\text{Au}^{3+}$ Metal Cations<sup>1</sup>

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**Abstract**—The complexation processes between  $\text{Fe}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Sn}^{4+}$ ,  $\text{Ce}^{3+}$  and  $\text{Au}^{3+}$  metal cations with macrocyclic ligand, 4'-nitrobenzo-15-crown-5(4'NB15C5), were studied in acetonitrile (AN), methanol (MeOH) and nitromethane (NM) solvents at different temperatures using conductometric method. The conductance data show that the stoichiometry of the complexes formed between this macrocyclic ligand and  $\text{Cd}^{2+}$ ,  $\text{Au}^{3+}$  cations is 1:1 (ML), but in the case of  $\text{Fe}^{3+}$ ,  $\text{Y}^{3+}$  and  $\text{Ce}^{3+}$  metal cations, 2: 1 ( $\text{M}_2 : \text{L}$ ) and 2: 2 [ $\text{M}_2 : \text{L}_2$ ] complexes are formed in nitromethane solutions. The results show, that the selectivity of 4'NB15C5 for the studied metal cations in methanol solutions at 15°C is:  $\text{Sn}^{4+} > \text{Cd}^{2+} > \text{Y}^{3+} > \text{Fe}^{3+} \approx \text{Ce}^{3+} > \text{Au}^{3+}$ , but in the case of acetonitrile, the stability order was found to be:  $\text{Y}^{3+} > \text{Au}^{3+} > \text{Fe}^{3+} > \text{Cd}^{2+}$ . The values of stability constants of the 1:1 [M:L] complexes were determined from conductometric data using a GENPLOT computer program. The values of thermodynamic parameter ( $\Delta H_c^\circ$  and  $\Delta S_c^\circ$ ) for formation of the complexes were obtained from temperature dependence of the stability constants, using the van't Hoff plots. The results show that the values of standard enthalpy ( $\Delta H_c^\circ$ ) and standard entropy ( $\Delta S_c^\circ$ ) change with the nature of the non aqueous solvents.

**Key words:** 4'-nitrobenzo-15-crown-5,  $\text{Fe}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Sn}^{4+}$ ,  $\text{Ce}^{3+}$  and  $\text{Au}^{3+}$  cations, Acetonitrile, Methanol, Nitromethane, Conductometry.

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## 1. INTRODUCTION

Conductance measurements of an electrolyte solution in the presence of a crown compound provide two valuable pieces of information. The first, is detection of complexation between the crown compound and the cation. Furthermore, the stability constant of the crown compound—cation complex can be determined from the conductance data. Macrocyclic design parameters, such as cavity size, the type and the number of donor atoms, the type and the number of proton-ionizable groups within and without the macrocyclic cavity, chirality's, the substituent groups, and steric hindrance and also the solvent parameters can all be used to obtain the desired selectivities [1, 2].

Today, the chemistry of the crown compounds forms an important part of the literature [3, 4]. Some of the papers deal with their applications such as ionophores in the construction of ion selective electrode [5–7], in ion exchange membrane [8, 9], in the preparation and preconcentration of the metal cations [10] and in the recovery of rare earth metal elements [11, 12].

The goal of the present investigation is to study the effect of nature of the cations and especially the solvent properties on the stoichiometry, stability and also the selectivity of the complexes formed between 4'-nitrobenzo-15-crown-5 and  $\text{Fe}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Sn}^{4+}$ ,  $\text{Ce}^{3+}$  and  $\text{Au}^{3+}$  metal cations in methanol, acetonitrile and nitromethane using the conductometric technique.

## 2. EXPERIMENTAL

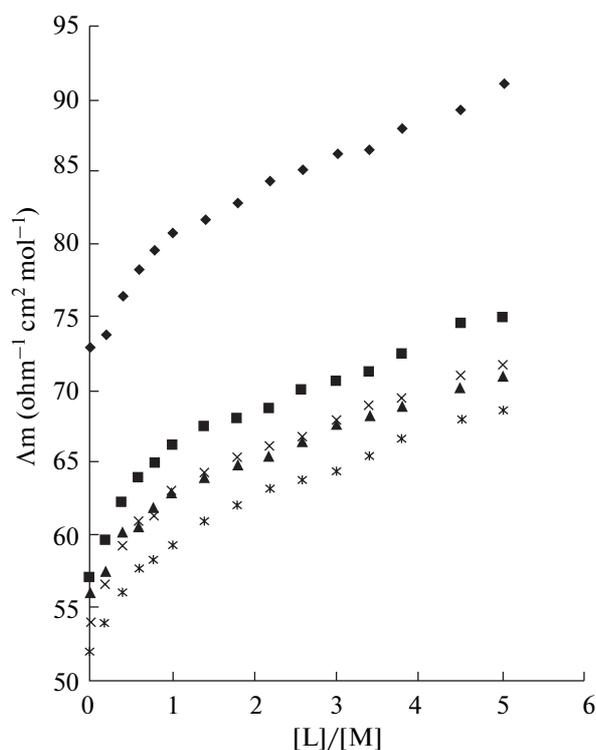
### 2.1. Material

4'-Nitrobenzo-15C5 (Merck), thin chloride ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ), cadmium nitrate ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), iron nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ), gold chloride ( $\text{AuCl}_3 \cdot \text{H}_2\text{O}$ ), yttrium nitrate ( $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ), cerium nitrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) methanol ( $\text{CH}_3\text{OH}$ ), acetonitrile ( $\text{CH}_3\text{CN}$ ) and nitromethane ( $\text{CH}_3\text{NO}_2$ ) (all from Merck) were used with the highest purity.

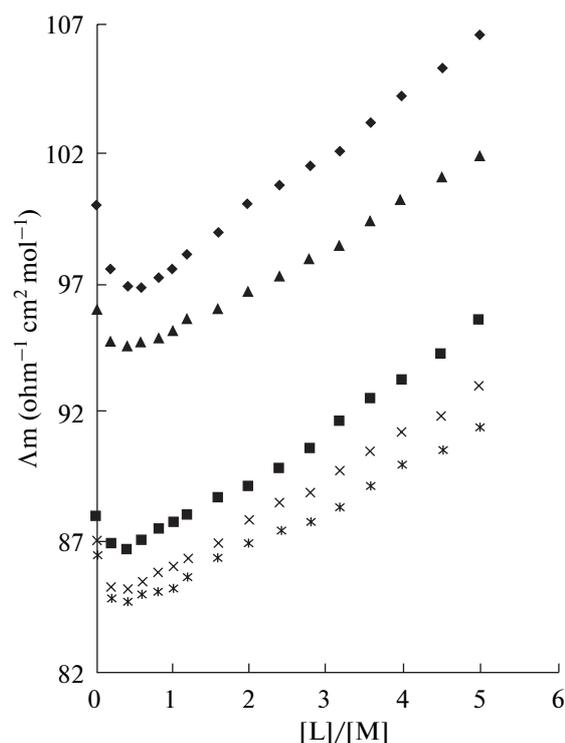
### 2.2. Procedure

The experimental procedure used to obtain the stability constants of the complexes is as follows: a solu-

<sup>1</sup> The article is published in the original.



**Fig. 1.** Molar conductance-mole ratio plots for (4'NB15C5 · Cd<sub>2+</sub>) complex in NM at 15°C (\*), 25°C (x), 35°C (▲), 45°C (■) and 55°C (◆).



**Fig. 2.** Molar conductance-mole ratio plots for complexation of 4'NB15C5 with Fe<sup>3+</sup> cation in NM at 15°C (\*), 25°C (x), 35°C (▲), 45°C (■) and 55°C (◆).

tion of metal salt ( $10^{-4}$  M) was placed in a titration cell and the conductance of solution was measured, then a step-by-step increase in the crown ether concentration was carried out by a rapid transfer from crown ether solution prepared in the same solvent ( $2 \times 10^{-3}$  M) 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 using a digital Amel conductivity apparatus, Model 160, in a water-bath thermostated at a constant temperature maintained within  $\pm 0.1^\circ\text{C}$ .

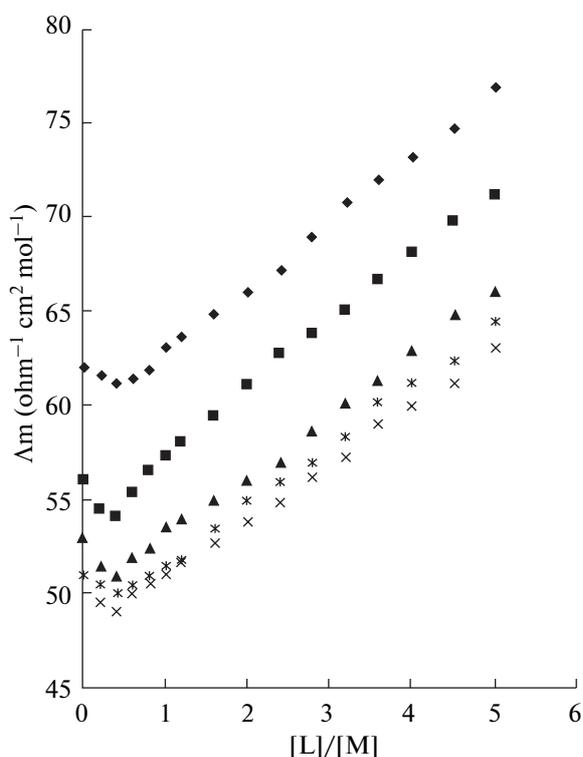
### 3. RESULTS AND DISCUSSION

The changes of molar conductance ( $\Lambda_m$ ) versus the ligand to the cation molar ratios ( $[L]_V/[M]_V$ ) for complexation of 4'NB15C5 with Fe<sup>3+</sup>, Y<sup>3+</sup>, Cd<sup>2+</sup>, Sn<sup>4+</sup>, Ce<sup>3+</sup> and Au<sup>3+</sup> metal cations in methanol, acetonitrile and nitromethane were studied at different temperatures. Four typical series of molar conductance values as a function of ligand/metal cation mole ratios in NM and AN solvents are shown in Figs. 1–4.

The stability constants of the 4'NB15C5 crown ether complexes at each temperature were calculated from variation of molar conductance as a function of ligand/metal cation mole ratios using a GENPLOT computer program. The values of the stability con-

stants ( $\log K_f$ ) for the 4'NB15C5 · M<sup>n+</sup> (M<sup>n+</sup> = Fe<sup>3+</sup>, Y<sup>3+</sup>, Cd<sup>2+</sup>, Sn<sup>4+</sup>, Ce<sup>3+</sup> and Au<sup>3+</sup>) complexes in various solvent systems at different temperatures are listed in Table 1.

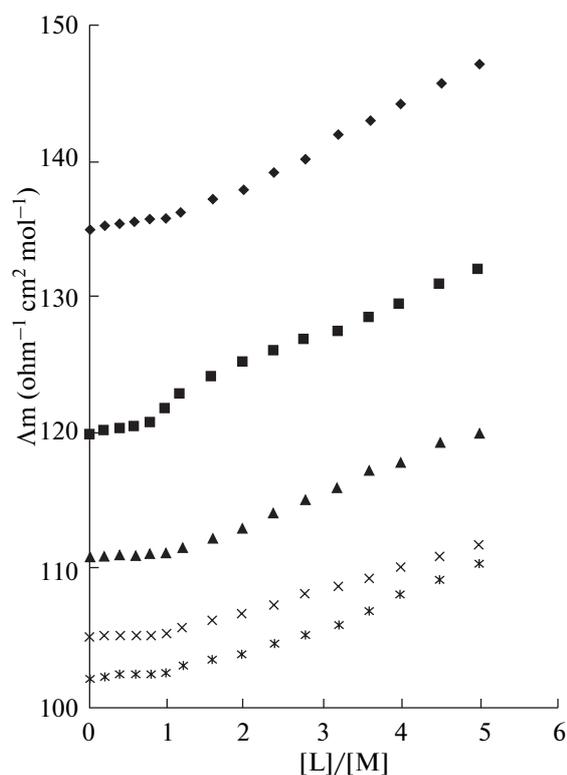
As is obvious from Fig. 1, addition of 4'NB15C5 crown ether to Cd<sup>2+</sup> ion in nitromethane solutions at different temperatures results in an increase in molar conductivity. This indicates that the (4'NB15C5 · Cd<sup>2+</sup>) complex in NM solvent is more mobile than free solvated Cd<sup>2+</sup> ion. The slope of the corresponding molar conductivity versus ligand/cation mole ratio plots changes sharply 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 Cd<sup>2+</sup> ion and 4'NB15C5 ligand in nitromethane solutions. But a gradual increase in the molar conductance was observed for some of the studied metal cations upon addition of the ligand to their solutions, which does not show a considerable change in the curvature of the plots at mole ratio 1, indicating that a weaker 1:1 [M:L] complex is formed in solutions. In most cases, as the temperature increases, the curvature of the mole ratio plots for complexation of 4'NB15C5 with the studied metal cations decreases which is an evidence for formation of stronger complexes at lower temperatures, therefore, the complexation processes are exothermic in these solvent systems and due to a decrease in viscosity of solvents with increasing temperature



1 **Fig. 3.** Molar conductance-mole ratio plots for complexation of 4'NB15C5 with  $\text{Y}^{3+}$  cation in NM at 15°C (\*), 25°C (x), 35°C (▲), 45°C (■) and 55°C (◆).

results in an increase the solvation of the dissolved species in solutions [13].

1 An interesting behaviour was observed for complexation of 4'NB15C5 with  $\text{Fe}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Sn}^{4+}$  and  $\text{Ce}^{3+}$  cations in nitromethane solutions. As is obvious from Figs. 2 and 3, addition of 4'NB15C5 to  $\text{Fe}^{3+}$  and  $\text{Y}^{3+}$  cations solutions at different temperatures causes the molar conductivity to initially decrease until the mole ratio reaches to 1/2 and then to increase. These graphical results indicate that 2: 1  $[\text{M}_2 : \text{L}]$  complexes are formed between 4'NB15C5 and  $\text{Fe}^{3+}$  and  $\text{Y}^{3+}$  cations in nitromethane solutions and these complexes are less mobile than free solvated  $\text{Fe}^{3+}$  and  $\text{Y}^{3+}$  cations. It seems that further addition of the ligand to  $[\text{M}_2 : \text{L}]$  complexes, causes formation of  $[\text{M}_2 : \text{L}_2]$  complexes with a club sandwich structure which are less solvated than  $[\text{M}_2 : \text{L}]$  complexes in nitromethane solutions and, therefore, the molar conductivity increases. Similar behaviour was observed for  $\text{Sn}^{4+}$  and  $\text{Ce}^{3+}$  cations in nitromethane solutions. Since the cavity size of 4'NB15C5 is not big enough to fit two  $\text{M}^{n+}$  ( $\text{M}^{n+} = \text{Fe}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Sn}^{4+}$  and  $\text{Ce}^{3+}$ ) cations, but it may suggest that the second  $\text{M}^{n+}$  cation probably interacts with the ligand via oxygen donor of  $-\text{NO}_2$  group and also with the  $\pi$  electron system of benzo group and, therefore, they form a 2: 1  $[\text{M}_2 : \text{L}]$  complex with the metal cations in nitromethane solutions and further addition of

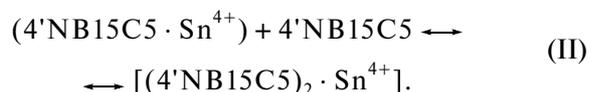
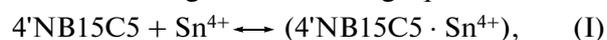


1 **Fig. 4.** Molar conductance-mole ratio plots for complexation of 4'NB15C5 with  $\text{Sn}^{4+}$  cation in MeOH at 15°C (\*), 25°C (x), 35°C (▲), 45°C (■) and 55°C (◆).

4'NB15C5 results in formation a  $[\text{M}_2 : \text{L}_2]$  complex with a club sandwich structure.

Since the donor number of methanol ( $\text{DN} = 20.0$ ) is bigger than those of acetonitrile ( $\text{DN} = 14.1$ ) and nitromethane ( $\text{DN} = 2.7$ ), therefore, the metal cations are much more solvated in this solvent in compared to the other two organic solvents. Therefore, as is obvious for Table 2, all of the metal cations form only 1:1  $[\text{M} : \text{L}]$  complexes with 4'-nitrobenzo-15-crown-5 in methanol solutions.

As is obvious from Fig. 4, addition of 4'NB15C5 to  $\text{Sn}^{4+}$  cation in acetonitrile solutions at different temperatures causes the molar conductivity to initially increase very slowly until the mole ratio reaches 1:1 and then to increase rapidly. Such behaviour may be described according to the following equilibria:



It seems that addition of the ligand to  $\text{Sn}^{4+}$  cation solution results in formation of a 1:1 complex (I) in which the mobility of the solvated complex is close to the mobility of free solvated  $\text{Sn}^{4+}$  cation, then addition of the second ligand to 1:1  $[\text{M} : \text{L}]$  complex, causes formation of a 1:2  $[\text{M} : \text{L}_2]$  complex with a sandwich structure which is less solvated than the 1:1 complex in

**Table 1.** Log $K_f$  values of (4'NB15C5 · Fe<sup>3+</sup>), (4'NB15C5 · Y<sup>3+</sup>), (4'NB15C5 · Cd<sup>2+</sup>), (4'NB15C5 · Sn<sup>4+</sup>), (4'NB15C5 · Ce<sup>3+</sup>) and (4'NB15C5 · Au<sup>3+</sup>) complexes in various solvents at different temperatures

Medium	Log $K_f \pm SD^a$				
	15°C	25°C	35°C	45°C	55°C
<b>(4'NB15C5 · Fe<sup>3+</sup>)</b>					
MeOH	4.0 ± 0.2	3.7 ± 0.1	2.7 ± 0.2	2.2 ± 0.4	2.1 ± 0.1
AN	2.9 ± 0.1	2.9 ± 0.1	2.9 ± 0.1	2.8 ± 0.2	b
NM	b	b	b		b
<b>(4'NB15C5 · Y<sup>3+</sup>)</b>					
MeOH	4.8 ± 0.1	3.7 ± 0.2	3.1 ± 0.3	2.8 ± 0.1	2.3 ± 0.1
AN	5.5 ± 0.1	4.8 ± 0.1	4.0 ± 0.1	2.0 ± 0.2	2.8 ± 0.2
NM	b	b	b	b	b
<b>(4'NB15C5 · Cd<sup>2+</sup>)</b>					
MeOH	5.0 ± 0.2	3.7 ± 0.1	b	b	b
AN	2.4 ± 0.6	2.1 ± 0.4	2.4 ± 0.5	2.0 ± 0.2	2.4 ± 0.4
NM	3.7 ± 0.1	3.9 ± 0.2	3.7 ± 0.1	3.9 ± 0.1	3.7 ± 0.1
<b>(4'NB15C5 · Sn<sup>4+</sup>)</b>					
MeOH	5.2 ± 0.4	2.7 ± 0.5	b	b	b
AN	b	b	b	b	b
NM	b	b	b	b	b
<b>(4'NB15C5 · Ce<sup>3+</sup>)</b>					
MeOH	4.0 ± 0.1	1.8 ± 0.2	1.7 ± 0.2	b	b
AN	b	b	b	b	b
NM	b	b	b	b	b
<b>(4'NB15C5 · Au<sup>3+</sup>)</b>					
MeOH	2.2 ± 0.2	b	b	b	b
AN	3.1 ± 0.1	2.5 ± 0.4	1.5 ± 0.1	1.0 ± 0.2	b
NM	b	4.8 ± 0.3	5.7 ± 0.2	4.6 ± 0.2	b

<sup>a</sup>SD: Standard deviation.<sup>b</sup>The data can not be fitted in equation

acetonitrile solutions and, therefore, the conductivity increases. The stoichiometric values for complexation of 4'NB15C5 with Fe<sup>3+</sup>, Y<sup>3+</sup>, Cd<sup>2+</sup>, Sn<sup>4+</sup>, Ce<sup>3+</sup> and Au<sup>3+</sup>

**Table 2.** Stoichiometric values of complexes ([M : L]) formed between 4'NB15C5 and various metal cations in non-aqueous solvents

	AN	NM	MeOH
Fe <sup>3+</sup>	[1 : 1]	[2 : 1], [2 : 2]	[1 : 1]
Y <sup>3+</sup>	[1 : 1]	[2 : 1], [2 : 2]	[1 : 1]
Cd <sup>2+</sup>	[1 : 1]	[1 : 1]	[1 : 1]
Sn <sup>4+</sup>	[1 : 1], [1 : 2]	[2 : 1], [2 : 2]	[1 : 1]
Ce <sup>3+</sup>	[1 : 1]	[2 : 1], [2 : 2]	[1 : 1]
Au <sup>3+</sup>	[1 : 1]	[1 : 1], [1 : 2]	[1 : 1]

metal cations in different non-aqueous solvents are summarized in Table 2.

The values of log $K_f$  for formation of (4'NB15C5 · Fe<sup>3+</sup>), (4'NB15C5 · Y<sup>3+</sup>), (4'NB15C5 · Cd<sup>2+</sup>), (4'NB15C5 · Sn<sup>4+</sup>), (4'NB15C5 · Ce<sup>3+</sup>) and (4'NB15C5 · Au<sup>3+</sup>) complexes in various solvent systems at different temperatures are given in Table 1. As is obvious from this Table, the order of stability of these complexes in methanol solutions at 15°C is:

(4'NB15C5 · Sn<sup>4+</sup>) > (4'NB15C5 · Cd<sup>2+</sup>) > (4'NB15C5 · Y<sup>3+</sup>) > (4'NB15C5 · Fe<sup>3+</sup>) ≈ 4'NB15C5 · Ce<sup>3+</sup> > (4'NB15C5 · Au<sup>3+</sup>), but in the case of acetonitrile, the stability sequence was found to be: (4'NB15C5) > (4'NB15C5 · Y<sup>3+</sup>) > (4'NB15C5 · Au<sup>3+</sup>) > (4'NB15C5 · Fe<sup>3+</sup>) > (4'NB15C5 · Cd<sup>2+</sup>).

This behaviour shows that the selectivity of 4'NB15C5 for the studied metal cations in solutions undergoes the solvent effect. The changes of log $K_f$  for

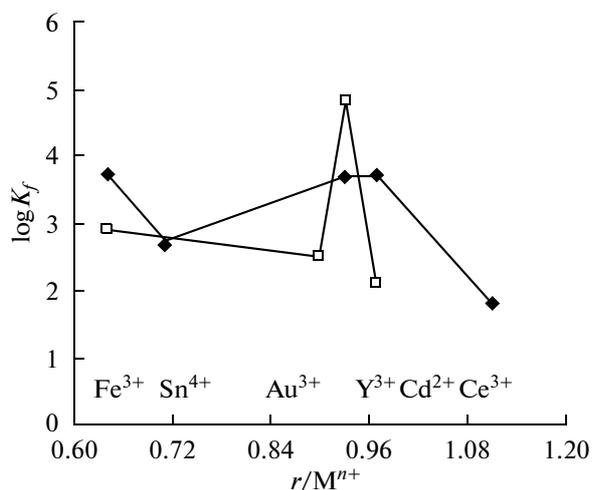


Fig. 5. Changes of  $\log K_f$  for (4'NB15C5 ·  $Fe^{3+}$ ), (4'NB15C5 ·  $Y^{3+}$ ), (4'NB15C5 ·  $Cd^{2+}$ ), (4'NB15C5 ·  $Sn^{4+}$ ), (4'NB15C5 ·  $Ce^{3+}$ ) and (4'NB15C5 ·  $Au^{3+}$ ) complexes versus the cationic radii at 15°C in MeOH ( $\blacklozenge$ ) and AN ( $\square$ ).

the complexes formed between 4'NB15C5 and  $Fe^{3+}$ ,  $Y^{3+}$ ,  $Cd^{2+}$ ,  $Sn^{4+}$ ,  $Ce^{3+}$  and  $Au^{3+}$  metal cations in methanol and acetonitrile solvents versus ionic radii are shown in Fig. 5. The  $Y^{3+}$  cation forms a more stable complex with 4'NB15C5 in AN than the other metal cations. Although the ionic radius size of  $Y^{3+}$  cation (0.93 Å) [14] is smaller than the size of the 4'NB15C5 cavity (1.7–2.7 Å) [14], but since the  $Y^{3+}$  cation is a harder acid than the other cations, therefore, the interaction of this cation with the oxygen atoms of 4'NB15C5 ligand is stronger than the other metal cations.

Assuming that the activity coefficients of the cation and complex have the same value,  $K_f$  is a thermodynamic equilibrium constant on the molar concentration scale, related to the Gibbs standard free energy of complexation reaction,  $\Delta G_c^\circ$ . The van't Hoff plots of  $\log K_f$  versus  $1/T$  for all of the investigated systems were constructed. For example the van't Hoff plots for (4'NB15C5 ·  $Au^{3+}$ ) and (4'NB15C5 ·  $Y^{3+}$ ) complexes in acetonitrile solutions are shown in Fig. 6.

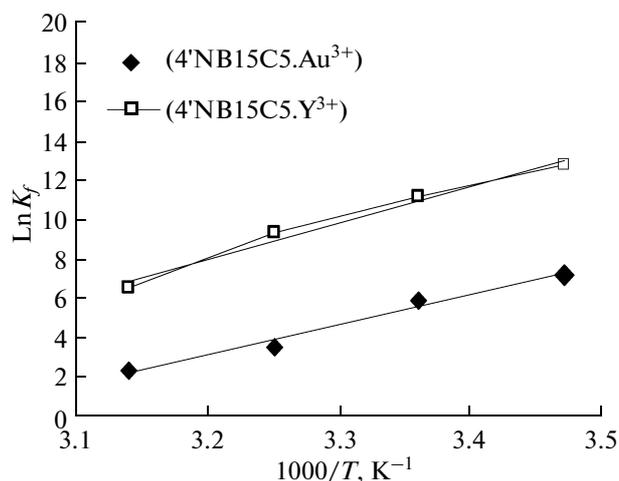


Fig. 6. Van't Hoff plots for (4'NB15C5 ·  $Au^{3+}$ ) ( $\blacklozenge$ ) and (4'NB15C5 ·  $Y^{3+}$ ) ( $\square$ ) complexes in AN.

The changes in standard enthalpy ( $\Delta H_c^\circ$ ) for the complexation reactions were obtained from the slope of the van't Hoff plots and the changes in standard entropy ( $\Delta S_c^\circ$ ) were calculated from the relationship  $\Delta G_{c,298.18}^\circ = \Delta H_c^\circ - 298.15 \Delta S_c^\circ$ . The thermodynamic data are summarized in Table 3. As is evident in this table, the complexation reactions between 4'NB15C5 and the studied metal cations in methanol and acetonitrile solvents are enthalpy stabilized and entropy destabilized and the values of standard enthalpy ( $\Delta H_c^\circ$ ) and standard entropy ( $\Delta S_c^\circ$ ) for these complexation processes change with the nature of non-aqueous solvents.

#### 4. CONCLUSIONS

The stability and selectivity of crown ether complexes with metal cations depend on several factors. These include the cavity size of the ligand, the character of the heteroatoms in the polyether ring, spatial distribution of the ring binding sites, the substituent

Table 3. Thermodynamic parameters for (4'NB15C5 ·  $Y^{3+}$ ) and (4'NB15C5 ·  $Au^{3+}$ ) complexes in various solvents at 25°C

	$\Delta G_c^\circ \pm SD^a$ (25°C) Kcal/mol	$\Delta H_c^\circ \pm SD^a$ Kcal/mol	$\Delta S_c^\circ \pm SD^a$ Cal/mol · K
(4'NB15C5 · $Y^{3+}$ )			
MeOH	$-5.1 \pm 0.2$	$-25 \pm 1.5$	$-67 \pm 4.9$
AN	$-6.6 \pm 0.3$	$-36.9 \pm 2.6$	$-101 \pm 8.6$
(4'NB15C5 · $Au^{3+}$ )			
AN	$-3.4 \pm 0.5$	$-21.6 \pm 1.3$	$-60.7 \pm 4.0$

<sup>a</sup>SD: Standard deviation.

group, and the diameter and nature of the cation. The results obtained in this work show that the order of stability of complexes formed between macrocyclic ligand 4'-nitrobenzo-15-crown-5 with  $\text{Fe}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Sn}^{4+}$ ,  $\text{Ce}^{3+}$  and  $\text{Au}^{3+}$  metal cations also changes with the nature of solvent. The conductometric measurements also reveal that the stoichiometry of the complexes formed between this macrocyclic ligand and the studied metal cations changes with the nature of the non-aqueous solvents. Therefore, the results obtained in this work show that the mechanism and the thermodynamics of complexation processes between macrocyclic ligands and metal cations and also the selectivity of these kinds of ligands for metal cations may be changed with the nature of non-aqueous solvents.

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SPELL: 1. complexation