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# A Conductometric Study of Complexation Reactions Between 4-Nitrobenzo-15-Crown-5 with $Ag^+$, $Hg^{2+}$, $Tl^+$ and $La^{3+}$ Metal Ions in Acetonitrile-Methanol Binary Solutions

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The complex formation between $Ag^+$, $Hg^{2+}$, $Tl^+$ and $La^{3+}$ metal ions with macrocyclic ligand, 4-nitrobenzo-15-crown-5 (NB15C5) was studied in acetonitrile (AN)-methanol (MeOH) binary systems at different temperatures using conductometric method. The obtained results show that the stoichiometry of the complexes is 1:1 (ML), but in the case of $Hg^{2+}$ cation, in addition to a 1:1 complex, a 1:2 ($ML_2$) complex is formed in solutions. The stability constants of the complexes were obtained from fitting of molar conductivity curves using a computer program, Genplot. A non-linear behaviour was observed for changes of log $K_f$ of the complexes *versus* the composition of AN-MeOH binary solution. The results show that the selectivity of NB15C5 for the metal cations changes with the composition of the mixed solvent. The values of standard enthalpy changes ($\Delta H^\circ_c$) for complexation reactions were obtained from the slope of the van't Hoff plots and the changes in standard entropy ($\Delta S^\circ_c$) were calculated from the relationship: $\Delta G^{\circ c,\ 298.15} = \Delta H^\circ_c - 298.15\ \Delta S^\circ_c$. The obtained results show that the complexes are entropy stabilized but from the enthalpy view point, depending on the solvent system the metal ion complexes are stabilized or destabilized and the values of $\Delta H^\circ_c$ and $\Delta S^\circ_c$ depend strongly on the nature of the medium.

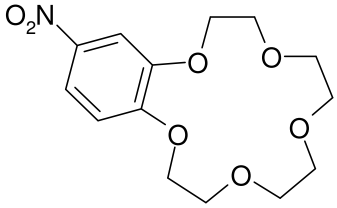
**Key Words: $Ag^+$, $Hg^{2+}$, $Tl^+$, $La^{3+}$, 4-Nitrobenzo-15-crown-5, Acetonitrile-methanol binary mixtures, Conductometry.**

## INTRODUCTION

Increased use of metals and chemicals in process industries has resulted in generation of large quantities of effluent that contain high level of toxic heavy metals and their presence poses environmental disposal problems due to their non-degradable and persistence nature.

Pollution by toxic heavy metals remains a serious environmental and public concern all over the world[1]. Various efficient technologies, including chemical precipitation[2], adsorption onto activated carbon[3], membrane processes[4] and ion exchange[5-7] were developed to improve their removal from the polluted media. These methods, however, display one or more limitations such as covering high operational costs or appearing to be insufficient to meet strict regulatory requirements as for chemical precipitation. To overcome these limitations, chemists have been devoted to developing materials capable of removing low concentrations of toxic metal ions such as polymers[8] or silicates[9], mesoporous molecular sieves[10] and metal complexing groups (*e.g.*, crown ethers[11,12]). Due to the specific affinity of heavy metals and complex groups on the sorbet surface, these sorbets exhibited enhanced sorption toward heavy metals however, the thermal and chemical stability of these complexes still needs further improvements.

In present study, the stability constants and thermodynamic quantities for complex formation of $Ag^+$, $Hg^{2+}$, $Tl^+$ and $La^{3+}$ metal ions by 4-nitrobenzo-15-crown-5 (NB15C5) in acetonitrile-methanol binary systems at different temperatures by conductometric method are determined.



Structure of 4-nitro-benzo-15-crown-5 (NB15C5)

## EXPERIMENTAL

Thallium nitrate (Prolabo), silver nitrate, lanthanum chloride (both from Merck), mercury(II) chloride (G.P.R) and 4-nitrobenzo-15-crown-5 (Fluka) was used without further purification. The solvents acetonitrile and methanol (both from Merck) were used with the highest purity.

The conductance measurements were performed on an AMEL model 60 conductometer in a water-bath thermostated with a constant temperature maintained within ± 0.03 °C. The electrolytic conductance was measured using a cell consisting of two platinum electrodes, which an alternating potential was applied. A conductometric cell with a cell constant of 0.73 $cm^{-1}$ was used throughout the studies.

**Formation constants of complexes:** A solution of metal cation salt ($1 \times 10^{-4}$ M) was placed in a titration cell, thermostated at a given temperature and the conductance of the solution was measured. A step-by-step increase in the crown ether concentration ($2 \times 10^{-3}$ M) was performed by a rapid transfer from crown ether solution prepared in the same solvent to the titration cell using a microburette. The conductance of the solution was measured after each addition at the desired temperature.

## RESULTS AND DISCUSSION

The changes of molar conductance ($\Lambda_m$) *versus* the ligand to cation mole ratio for the complexation of NB15C5 ligand with $Ag^+$, $Hg^{2+}$, $Tl^+$ and $La^{3+}$ metal ions in acetonitrile-methanol (AN-MeOH) binary systems were studied at different temperatures. The changes of $\Lambda_m$ *versus* ligand/cation mol ratio ($[L]_t/[M]_t$) for (NB15C5-$Hg^{2+}$) complex in pure AN and for (NB15C5-$La^{3+}$) complex in an AN-MeOH binary system (75 % mol of acetonitrile) are shown in Figs. 1 and 2, respectively.

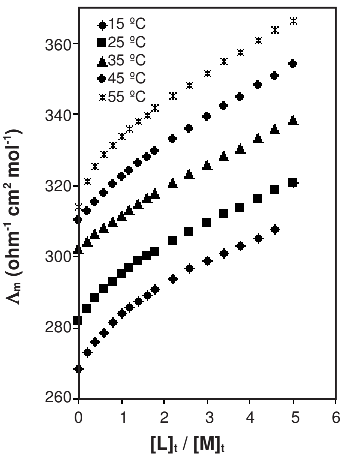


Fig. 1. Molar conductance-mole ratio plots for (NB15C5-$La^{3+}$) complex in AN-MeOH binary system (mol% AN = 75) at different temperatures

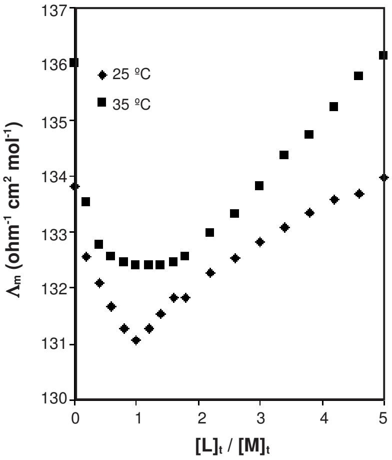


Fig. 2. Molar conductance-mole ratio plots for (NB15C5-$Hg^{2+}$) complex in pure AN at different temperatures

The stability constants of the crown ether complexes at each temperature were calculated from the changes of molar conductance as a function of ligand/cation mole ratios. The details of calculation of stability constant of complexes have been described earlier[13].

All calculated stability constants (log $K_f$) for 1:1 (NB15C5-$M^{n+}$) ($M^{n+}$ = $Ag^+$, $Hg^{2+}$, $Tl^+$ and $La^{3+}$) complexes in various solvent systems are listed in Table-1.

It is obvious, from Fig. 1 that addition of NB15C5 to $La^{3+}$ ion solution at different temperatures results in an increase in molar conductivity. This indicates that (NB15C5-$La^{3+}$) complex is more mobile than free solvated $La^{3+}$ cation. Similar behaviour was observed for $Ag^+$, $Hg^{2+}$ and $Tl^+$ cations in various solvent systems.

Addition of NB15C5 to $Hg^{2+}$ ion in pure AN at different temperatures (except at 15 °C) causes the molar conductivity to initially decreases until the mole ratio reaches 1:1 and then to increase (Fig. 2). Such behaviour may be described according to the following equilibria:

TABLE-1
log $K_f$ OF (NB15C5-$Ag^+$), (NB15C5-$Hg^{2+}$), (NB15C5-$Tl^+$) AND (NB15C5-$La^{3+}$) COMPLEXES IN AN-MeOH BINARY MIXTURES AT DIFFERENT TEMPERATURES

| Medium | log $K_f$ ± SD[a] | | | | |
|---|---|---|---|---|---|
| | 15 °C | 25 °C | 35 °C | 45 °C | 55 °C |
| **NB15C5-$Ag^+$** | | | | | |
| Pure AN | 3.56±0.05 | 3.14±0.08 | 3.59±0.11 | 3.23±0.04 | 3.25±0.04 |
| 75 % AN-25 % MeOH[b] | 3.40±0.06 | 3.32±0.05 | 3.31±0.10 | 3.19±0.03 | 3.07±0.06 |
| 50 % AN-50 % MeOH | 3.77±0.05 | 3.06±0.07 | 3.07±0.05 | 3.10±0.05 | 3.05±0.10 |
| 25 % AN-75 % MeOH | 3.30±0.04 | 2.75±0.04 | 2.62±0.08 | d | d |
| Pure MeOH | 3.44±0.09 | 2.63±0.15 | d | d | d |
| **NB15C5-$Hg^{2+}$** | | | | | |
| Pure AN | 3.45±0.05 | c | c | c | c |
| 75 % AN-25 % MeOH[b] | 2.83±0.04 | 2.89±0.05 | 2.95±0.08 | 2.87±0.06 | 3.45±0.03 |
| 50 % AN-50 % MeOH | 2.90±0.12 | 2.81±0.08 | 2.96±0.06 | 2.68±0.07 | 3.46±0.06 |
| 25 % AN-75 % MeOH | 2.76±0.07 | 2.77±0.08 | 2.76±0.12 | 2.84±0.04 | 3.17±0.04 |
| Pure MeOH | 3.35±0.04 | 3.41±0.04 | 3.60±0.03 | 3.22±0.07 | 3.27±0.04 |
| **NB15C5-$Tl^+$** | | | | | |
| Pure AN | 3.52±0.02 | 3.35±0.02 | 3.22±0.03 | 3.21±0.03 | 3.21±0.04 |
| 75 % AN-25 % MeOH[b] | 3.87±0.11 | 3.60±0.11 | 3.15±0.12 | 3.12±0.10 | 3.38±0.08 |
| 50 % AN-50 % MeOH | 3.49±0.10 | 3.23±0.09 | 2.97±0.10 | 3.12±0.07 | 2.88±0.06 |
| 25 % AN-75 % MeOH | 3.67±0.06 | 3.31±0.05 | 2.71±0.08 | 2.81±0.10 | 2.86±0.06 |
| Pure MeOH | 3.42±0.04 | 2.75±0.08 | 2.89±0.08 | 3.18±0.07 | 2.85±0.08 |
| **NB15C5-$La^{3+}$** | | | | | |
| Pure AN | 2.81±0.10 | 2.74±0.10 | 2.83±0.10 | 2.79±0.11 | 2.62±0.10 |
| 75 % AN-25 % MeOH[b] | 3.49±0.10 | 3.14±0.06 | 4.00±0.01 | 3.41±0.06 | 3.60±0.06 |
| 50 % AN-50 % MeOH | 3.83±0.06 | 3.05±0.08 | 3.23±0.06 | 2.91±0.10 | 2.81±0.10 |
| 25 % AN-75 % MeOH | 3.07±0.06 | 2.74±0.07 | 2.71±0.10 | 2.72±0.01 | d |
| Pure MeOH | 3.08±0.06 | 3.10±0.05 | 2.98±0.05 | 2.88±0.04 | 3.21±0.05 |

[a]SD = standard deviation. [b]The composition of binary solvents is expressed in mol % of each solvent. [c]The data can not be fitted in equation. [d] $K_f$ is very weak.

$$(Hg^{2+}, 2Cl^-) + NB15C5 \rightleftharpoons Hg^{2+}.NB15C5, 2Cl^- \qquad (I)$$

$$Hg^{2+}.NB15C5, 2Cl^- + NB15C5 \rightleftharpoons Hg^{2+}.(NB15C5)_2 + 2Cl^- \qquad (II)$$

It seems that addition of the ligand to mercury ion solution results in formation of relatively stable 1:1 complex (I) which is present as an ion-pair, then addition of the second ligand to ion pair complex, causes formation of a stable 1:2 complex with a sandwich structure (II) which decreases the space for diffusion and interaction of $Cl^-$ ion with mercury cation and results in dissociation of ion pair therefore, the conductivity increases. These results show that the stoichiometry and mechanism of the complex formation change with the composition of the mixed solvent. Similar behaviour has been observed by Takeda and his co-workers in their study of complex formation between 18C6 with Li$^+$, K$^+$ and Rb$^+$ ions[14] and also in the reaction of complex formation between DC18C6 ligand with Tl$^+$ cation[15] in non-aqueous solvents.

The changes of log K$_f$ *versus* the mole fraction of MeOH for (NB15C5-Hg$^{2+}$) complex in AN-MeOH binary systems at different temperatures is shown in Fig. 3 and the changes of stability constants of (NB15C5-Ag$^+$), (NB15C5-Hg$^{2+}$), (NB15C5-Tl$^+$) and (NB15C5-La$^{3+}$) complexes as a function of cationic radii in various AN-MeOH binary systems are shown in Figs. 4 and 5.

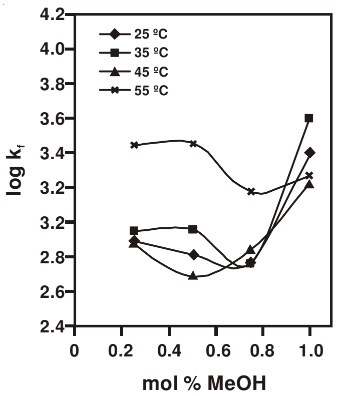


Fig. 3. Changes of stability constant (log K$_f$) of (NB15C5-Hg$^{2+}$) complex with the composition of AN-MeOH binary system at different temperatures

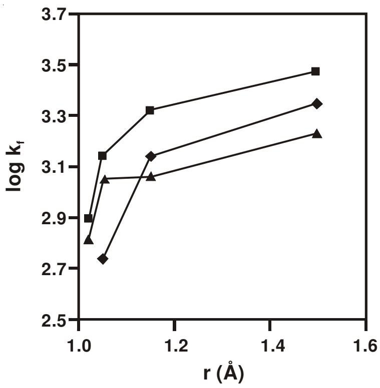


Fig. 4. Changes of log K$_f$ for (NB15C5-Ag$^+$), (NB15C5-Hg$^{2+}$), (NB15C5-Tl$^+$) and (NB15C5-La$^{3+}$) complexes *versus* cationic radii in various mixed solvents systems at 25 ºC: mol % MeOH = 25.3 (■), mol % MeOH = 50 (▲) and mol % MeOH = 75 (◆)

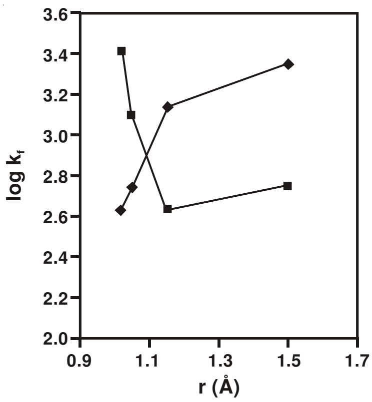


Fig. 5. Changes of log K$_f$ for (NB15C5-Ag$^+$), (NB15C5-Hg$^{2+}$), (NB15C5-Tl$^+$) and (NB15C5-La$^{3+}$) complexes versus cationic radii at 25 ºC: in pure AN (◆) and pure MeOH (■)

The changes of log $K_f$ *vs.* the mole fraction of MeOH for ($NB15C5-Hg^{2+}$) complex in AN-MeOH binary system at different temperatures is shown in Fig. 3. The non-linear behaviour is observed for the stability constant (log $K_f$) of ($NB15C5-Hg^{2+}$) complex with the composition of AN-MeOH binary system, may be due to strong interactions between the constituent solvents which resulted in some of the chemical and physical properties of each of solvent such as acidity, basicity, polarity, relative permittivity[16] and even the structure of the solvent molecules change when they mixed with one another and, therefore, changing their solvating ability towards the metal cations, ligand and the resulting complexes. The results obtained by Venables *et al.*[17] clearly demonstrate that there is a significant amount of hydrogen bonding between methanol and acetonitrile molecules. A non-monotonic behaviour was also observed for the other metal-ion complexes in these binary solutions.

Figs. 4 and 5 show that the selectivity order of these metal-ion complexes at 25 °C changes with the composition of AN-MeOH binary systems. It is interesting to note that the selectivity order of the complexes in two mixtures of AN-MeOH binary system with 50 and 75 mol % of AN is: ($NB15C5-Tl^{+}$) > ($NB15C5-Ag^{+}$) > ($NB15C5-La^{3+}$) > ($NB15C5-Hg^{2+}$). The $Tl^{+}$ ion forms the most stable complex with NB15C5, because it is bounded in the complex by an ion-dipole interaction with a covalent contribution[18]. But in the case of 25 mol % AN, the selectivity order changes to: ($NB15C5-Tl^{+}$) > $NB15C5-Hg^{2+}$) > ($NB15C5-Ag^{+}$) > ($NB15C5-La^{3+}$).

The changes in standard enthalpy ($\Delta H^\circ_c$) for complexation reactions were determined in the usual manner from the slopes of the van't Hoff plots and the changes in standard entropy ($\Delta S^\circ_c$) were calculated from the relationship: $\Delta G^\circ_c$, 298.15 = $\Delta H^\circ_c$ - 298.15 $\Delta S^\circ_c$. The results are summarized in Table-2.

The data in Table-2 showed that in most cases, the complexation reactions between NB15C5 and $Ag^{+}$, $Hg^{2+}$, $Tl^{+}$ and $La^{3+}$ metal ions in AN-MeOH binary systems are entropy stabilized but depending on the solvent system, the metal ion complexes are enthalpy stabilized or destabilized. As is obvious from Figs. 6 and 7, both of these thermodynamic parameters ($\Delta H^\circ_c$ and $\Delta S^\circ_c$) change non-monotonically with the composition of the mixed solvent. The anomalous behaviour which is observed for changes of these thermodynamic quantities *vs.* the composition of AN-MeOH binary solution, may be related to changes occurring in the structure of the solvent mixtures due to formation of hydrogen bond between these two dipolar protic and aprotic solvents and, therefore, changing the structure of solvent system which resulted in changing the solvation number of the dissolved species in solutions.

TABLE-2
THERMODYNAMIC PARAMETERS FOR (NB15C5-Ag$^{+}$), (NB15C5-Hg$^{2+}$), (NB15C5-Tl$^{+}$) AND (NB15C5-La$^{3+}$) COMPLEXES IN AN-MeOH BINARY MIXTURES

| Medium | $-\Delta G^{o}_{c} \pm SD^{a}$ (kcal mol$^{-1}$) | $-\Delta H^{o}_{c} \pm SD^{a}$ (kcal mol$^{-1}$) | $-\Delta S^{o}_{c} \pm SD^{a}$ (cal mol$^{-1}$) |
|---|---|---|---|
| **NB15C5-Ag$^{+}$** | | | |
| Pure AN | 4.30±0.11 | 1.65±0.23 | 14.41±0.74 |
| 75 % AN-25 % MeOH$^{b}$ | 4.54±0.12 | 3.48±0.54 | 15.21±1.77 |
| 50 % AN-50 % MeOH | 4.18±0.09 | – | 14.01±0.62 |
| 25 % AN-75 % MeOH | 3.75±0.06 | 14.53±4.46 | – |
| **NB15C5-Hg$^{2+}$** | | | |
| 75 % AN-25 % MeOH$^{b}$ | 3.95±0.06 | 6.51±1.94 | 13.26±6.40 |
| 50 % AN-50 % MeOH | 3.82±0.12 | -7.34±0.45 | 12.80±1.47 |
| 25 % AN-75 % MeOH | 3.78±0.01 | 1.21±0.40 | 12.68±1.30 |
| Pure MeOH | 4.66±0.06 | 5.43±1.43 | 15.66±4.63 |
| **NB15C5-Tl$^{+}$** | | | |
| Pure AN | 4.58±0.03 | -6.25±0.38 | 15.34±1.27 |
| 75 % AN-25 % MeOH$^{b}$ | 4.92±0.18 | -11.16±2.49 | – |
| 50 % AN-50 % MeOH | 4.40±0.12 | 6.61±1.71 | 14.79±5.65 |
| 25 % AN-75 % MeOH | 4.27±0.07 | -19.92±0.52 | 14.26±1.75 |
| Pure MeOH | 3.76±0.10 | 9.15±1.70 | 12.65±5.57 |
| **NB15C5-La$^{3+}$** | | | |
| Pure AN | 3.75±0.14 | – | 12.57±0.46 |
| 75 % AN-25 % MeOH$^{b}$ | 4.49±0.09 | -6.03±2.35 | 15.02±7.78 |
| 50 % AN-50 % MeOH | 4.41±0.01 | -11.58±0.95 | 14.75±3.18 |
| 25 % AN-75 % MeOH | 3.63±0.10 | – | 12.20±0.36 |
| Pure MeOH | 4.21±0.08 | -4.46±1.77 | 14.10±0.58 |

[a] SD = Standard deviation. [b] The composition of binary solvents is expressed in mol % of each solvent. –With high uncertainty.

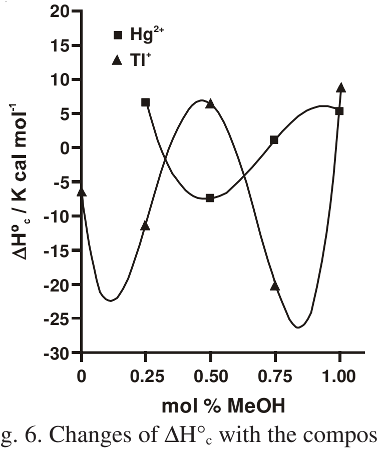


Fig. 6. Changes of $\Delta H^{\circ}_{c}$ with the composition of the AN-MeOH binary system for formation of (NB15C5-Hg$^{2+}$) (■) and (NB15C5-Tl$^{+}$) (▲) complexes

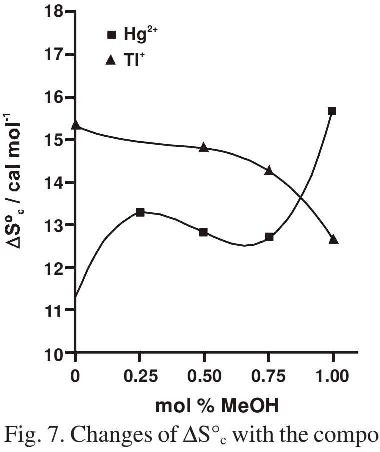


Fig. 7. Changes of $\Delta S^{\circ}_{c}$ with the composition of the AN-MeOH binary systems for formation of (NB15C5-Hg$^{2+}$) (■) and (NB15C5-Tl$^{+}$) (▲) complexes

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