Conductometric Studies of Solvent Influence upon Complex Formation Between 4′-Nitrobenzo-15-crown-5 and Ni²⁺, Co²⁺ and Cu²⁺ in Acetonitrile-Methanol Binary Mixtures

F. Boosaeeidi, G.H. Rounaghi* and A. Ghaemi
Department of Chemistry, Faculty of Sciences
Ferdowsi University of Mashhad, Mashhad, Iran
E-mail: ghrounaghi@yahoo.com

The complex formation between Ni^{2+}, Co^{2+} and Cu^{2+} metal cations with 4′-nitrobenzo-15-crown-5 was studied in aceto-nitrile (AN)-methanol (MeOH) binary systems at different temperatures using conductometric method. In all cases, 4′-nitrobenzo-15-crown-5 forms 1:1 complexes with these metal ions. The stability of the complexes is sensitive to the solvent composition and non-linear behaviour was observed for variation of log k_f of the complexes *versus* the composition of the binary mixed solvents. The results show that the selectivity order of 4′-mitrobenzo-15-crown-5 for the metal ions in pure AN is: $Co^{2+} > Cu^{2+} > Ni^{2+}$, but in the case of pure MeOH is: $Ni^{2+} > Cu^{2+} > Co^{2+}$ and this selectivity order is changed with the composition of the mixed solvents. The values of thermodynamic parameters ($\Delta H^\circ c$, $\Delta S^\circ c$) for comple-xation reactions were obtained from temperature dependence of the stability constants and the results show that in most cases, the complexes are enthalpy stabilized, but entropy destabilized and the values of $\Delta H^\circ c$ and $\Delta S^\circ c$ depend strongly on the nature of the medium. A non-linear behaviour is observed between the thermodynamic parameters and the composition of the mixed solvents.

Key Words: 4′-Nitrobenzo-15-crown-5, Ni²⁺, Co²⁺, Cu²⁺, Acetonitrile-methanol binary mixtures, conductometry.

INTRODUCTION

Pedersen's[1] early investigations of the host-guest chemistry of macro-cyclic crown ethers has led to an explosion of interest in their use as host systems for the study of molecular recognition and inclusion phenomena. Numerous applications of crown ethers arise from their ability to enter into selective complexation with alkali metal cations and to transport these species selectivity across liquid membranes[2,3].

As such crown ethers have been utilized for constructing amperometry[4,5] potentiometry[6], fluorescence[7,8] and surface techniques[9] based sensors for selective detection of cationic, anionic and also neutral analytes[10,11].

Obviously, the cation-binding and extraction ability of crown ethers is critically affected by several factors including the symmetry of the crown ether, the size-fit relationship, the type of the donor atoms, multiplicity and cooperative effects of neighbouring binding sites. The preorganization of a host molecule toward a certain guest compound is a central determinant of binding power and one of the most important strategies to increase complexing ability and selectivity[12].

Studies of crown ether complexes in various solvents show that the thermodynamic and kinetic parameters for complexation processes are affected by the nature and composition of the solvent system[13,14].

In this paper, the results of thermodynamic study for complexation reactions between 4′-nitrobenzo-15-crown-5 with Ni^{2+}, Co^{2+} and Cu^{2+} in AN-MeOH binary mixtures at different temperatures using conductometric method is reported.

EXPERIMENTAL

4′-Nitrobenzo-15-crown-5 (Fluka), copper(II) nitrate, nickel(II) nitrate and cobalt(II) perchlorate all from Merck were used without further purification. Acetonitrile and methanol (both from Merck) were used with the highest purity.

The experimental procedure to obtain the formation constants of complexes is as follows: a solution of metal 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 in the crown ether concentration was performed by a rapid transfer from crown ether (2.0×10^{-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 60 in a water bath thermostated at a constant temperature within 0.03 ºC.

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 variation of molar conductance (Λ_m) *versus* the ligand to the cation molar ratio ([L]$_t$/[M]$_t$) for complexation of 4′-nitrobenzo-15-crown-5 with Ni^{2+}, Co^{2+} and Cu^{2+} in AN-MeOH binary systems were studied at different temperatures. [L]$_t$ is the total concentration of 4′-nitrobenzo-15-crown-5 and [M]$_t$ is the total concentration of each metal cation in solution. As an example, the variation of Λ_m *vs.* [L]$_t$/[M]$_t$ for (4′-nitrobenzo-15C5 Ni)$^{2+}$ complex in pure AN is shown in Fig. 1.
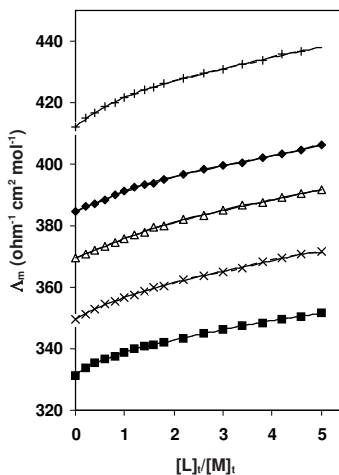
Fig. 1.   Molar conductance-mole ratio plots for (4′-nitrobenzo-15C5. Ni)$^{2+}$
complex in pure acetonitrile at different temperatures (ºC): (■ 15,
× 25, ▲ 35, ◆ 45, + 55)

As seen from Fig. 1, addition of 4′-nitrobenzo-15C5 to a solution of
Ni^{2+} cation in pure acetonitrile at different temperatures results in an increase
in molar conductivity. This indicates that (4′-nitrobenzo-15C5 Ni)$^{2+}$ complex
is more mobile than free solvated Ni^{2+} cation. Similar behaviour was observed
for Co^{2+} and Cu^{2+} cations in various solvent systems. The slope of the corres-
ponding molar conductivity *vs.* ligand/metal cation plots 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. Somewhat similar behaviour
was observed for Co^{2+} and Cu^{2+} cations in the binary mixed solvents.

The stability constants of the 4′-nitrobenzo-15C5 complexes at each
temperature were calculated from the variation of molar conductance as a
function of $[L]_t/[M]_t$ molar ratio using a GENPLOT computer program[15].
The details of the calculation of the stability constants of complexes by
conductometric method has been described elsewhere[16]. The stability con-
stants (log k_f) for (4′-nitrobenzo-15C5 M)$^{2+}$ (M^{2+} = Ni^{2+}, Co^{2+} and Cu^{2+})
complexes in various solvent systems are listed in Table-1.

The van't Hoff plots of log k_f *versus* 1/T for all investigated systems
were constructed. The changes in standard enthalpy (ΔHºc) were obtained
from the slope of the van't Hoff plots and the changes in standard entropy
(ΔSºc) were calculated from the relationship ΔHº$_{298.15}$ = ΔHºc - 298.15 ΔSºc.
The thermodynamic data are summarized in Table-2. In most cases, the
complexation reactions between 4′-nitrobenzo-15C5 and the studied metal
cations in AN-MeOH binary solutions are enthalpy stabilized but entropy
destabilized.

TABLE-1
log K_f VALUES OF (4′-NITROBENZO-15C5 Ni)$^{2+}$, (4′-NITROBENZO-15C5 Co)$^{2+}$
AND (4′-NITROBENZO-15C5 Cu)$^{2+}$ COMPLEXES IN AN-MeOH BINARY
MIXTURES AT DIFFERENT TEMPERATURES

Medium	log K_f ± SD[a]				
	15 ℃	25 ℃	35 ℃	45 ℃	55 ℃
(4′-Nitrobenzo-15C5 Ni)$^{2+}$ [b]					
Pure AN	3.44±0.06	3.25±0.05	3.19±0.04	3.22±0.06	3.52±0.06
75%AN-25%MeOH[c]	4.00±0.12	3.83±0.07	3.48±0.07	3.15±0.09	3.18±0.05
50%AN-50%MeOH	3.99±0.03	3.87±0.12	3.67±0.11	3.88±0.07	3.43±0.08
25%AN-75%MeOH	3.82±0.07	4.07±0.08	3.49±0.10	3.63±0.10	3.47±0.06
Pure MeOH	3.74±0.07	3.66±0.07	3.54±0.05	3.32±0.05	3.41±0.08
(4′-Nitrobenzo-15C5 Co)$^{2+}$ [b]					
Pure AN	4.29±0.06	3.94±0.07	4.04±0.07	3.49±0.13	3.75±0.08
75%AN-25%MeOH[c]	3.78±0.11	4.08±0.09	3.82±0.08	3.61±0.10	4.04±0.13
50%AN-50%MeOH	3.66±0.10	3.82±0.08	3.53±0.10	3.49±0.10	4.01±0.09
25%AN-75%MeOH	3.71±0.06	3.59±0.06	3.31±0.07	3.37±0.10	3.82±0.10
Pure MeOH	3.12±0.09	3.27±0.07	3.30±0.06	3.17±0.11	3.44±0.08
(4′-Nitrobenzo-15C5 Cu)$^{2+}$ [b]					
Pure AN	4.01±0.05	3.49±0.10	3.38±0.08	3.05±0.09	3.17±0.04
75%AN-25%MeOH[c]	3.44±0.08	3.78±0.06	3.33±0.06	3.24±0.03	3.23±0.06
50%AN-50%MeOH	3.48±0.08	2.98±0.11	2.72±0.11	2.67±0.18	3.13±0.05
25%AN-75%MeOH	4.07±0.06	3.47±0.04	3.45±0.10	3.32±0.08	3.61±0.06
Pure MeOH	3.55±0.07	3.32±0.06	3.15±0.04	2.94±0.06	2.68±0.09

[a]SD = standard deviation; [b]The concentration of each metal cation was 1.0×10^{-4} M;
[c]Composition of binary mixtures is expressed in mol% for each solvent system.

TABLE-2
THERMODYNAMIC PARAMETERS FOR (4′-NITROBENZO-15C5 Ni)$^{2+}$,
(4′-NITROBENZO-15C5 Co)$^{2+}$ AND (4′-NITROBENZO-15C5 Cu)$^{2+}$ COMPLEXES IN
AN-MeOH BINARY MIXTURES

Medium	-ΔG°c ± SD[a] (25℃) (KJ/mol)	-ΔH°c ± SD[a] (KJ/mol)	-ΔS°c ± SD[a] (J/mol K)
(4′-Nitrobenzo-15C5 Ni)$^{2+}$ [b]			
Pure AN	18.57±0.27	-21.12±5.32	-62.34±17.79
75.5%AN-25.0%MeOH[b]	21.89±0.37	-43.15±10.31	c
50.0%AN-50.0%MeOH	22.10±0.69	-27.02±5.07	-74.02±17.04
25.0%AN-75.0%MeOH	23.23±0.45	-14.72±4.07	-77.85±13.05
Pure MeOH	-21.00±0.38	-16.21±2.29	-70.38±7.67
(4′-Nitrobenzo-15C5 Co)$^{2+}$ [b]			
Pure AN	22.51±0.41	-24.94±1.50	-78.76±4.82
75.5%AN-25.0%MeOH[b]	23.30±0.53	-42.82±6.73	-78.30±2.16
50.0%AN-50.0%MeOH	21.81±0.44	15.46±2.99	-73.00±9.80
25.0%AN-75.0%MeOH	20.50±0.33	-20.37±4.41	-68.69±1.41
Pure MeOH	18.67±0.37	14.63±3.41	-62.65±11.31
(4′-Nitrobenzo-15C5 Cu)$^{2+}$ [b]			
Pure AN	19.93±0.57	-52.30±8.48	c
75.5%AN-25.0%MeOH[b]	21.54±0.34	-10.06±1.58	-72.20±5.15
50.0%AN-50.0%MeOH	17.00±0.67	-47.89±1.76	-56.87±36.91
25.0%AN-75.0%MeOH	19.81±0.23	-14.38±3.49	-66.38±11.31
Pure MeOH	18.96±0.35	-33.42±7.82	-63.49±2.58

[a]SD = standard deviation; [b]Composition of binary mixtures is expressed in mol% for each
solvent system; [c]With high uncertainty.

The changes of log k_f *versus* the mole fraction of AN for (4′-nitrobenzo-15C5 Cu)$^{2+}$ complex in AN-MeOH binary system at different temperatures are shown in Fig. 2 and the changes of the stability constants (log k_f) of (4′-nitrobenzo-15C5 Ni)$^{2+}$, (4′-nitrobenzo-15C5 Co)$^{2+}$ and (4′-nitrobenzo-15C5 Cu)$^{2+}$ complexes as a function of cationic radii in various AN-MeOH binary systems are shown in Fig. 3.
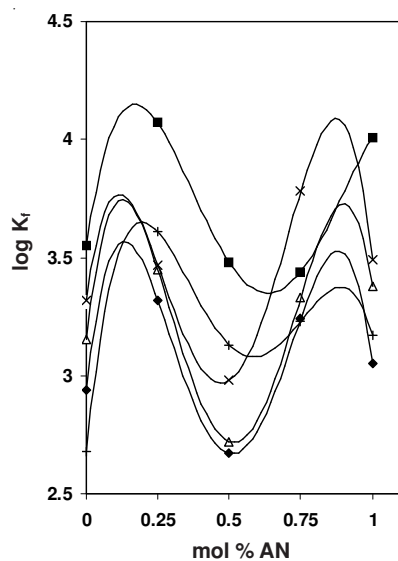

Fig. 2. Changes the stability constant of (4′-nitrobenzo-15C5 Cu)$^{2+}$ complex with the mole fraction of AN at different temperatures (ºC): (■ 15, × 25, ▲ 35, ◆ 45, + 55)
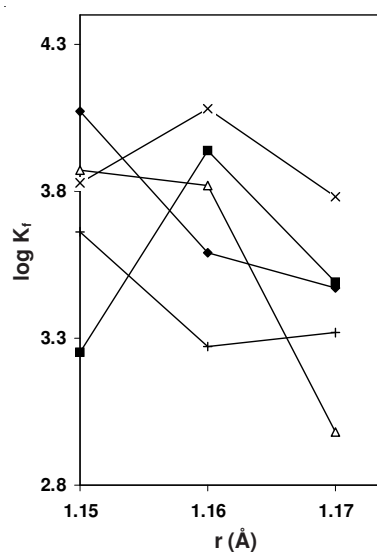
Fig. 3. Variation of log k_f for (4′-nitrobenzo-15C5 Ni)$^{2+}$, (4′-nitrobenzo-15C5 Co)$^{2+}$ and (4′-nitrobenzo-15C5 Cu)$^{2+}$ complexes *versus* cationic radii in various solvent systems at 25 ºC: (mol % AN = 100, ■ mol % AN = 75 ×, mol % AN = 50 ▲, mol % AN = 25 ◆, mol % MeOH = 100 +)

As obvious from Fig. 2, the variation of the stability constants of the (4′-nitrobenzo-15C5 Cu)$^{2+}$ complex *versus* the mole fraction of AN in AN-MeOH binary system, is non-linear. Similar behaviour was observed for (4′-nitrobenzo-15C5 Ni)$^{2+}$ and (4′-nitrobenzo-15C5 Co)$^{2+}$ complexes in AN-MeOH binary system. 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, cations and even the resulting complexes in these solvent mixtures. Some structural changes probably occur in the structure of the solvents when they mixed with one another. These structural changes may result in changing the interations of those solvents with the solutes. In addition, the heteroselective solvation of the cation, anion and

ligand and the character of its changes with the composition of the mixed solvents and temperature may be effective in these complexation processes. Parasad and co-workers[17] have studied the interactions between acetonitrile and methanol molecules by excess adiabatic compressibility (β^E) and excess intermolecular free length (L^E_f) measurements at 303.15 K and showed that these parameters become increasingly negative with increasing strength of interaction between the component molecules. In addition, it has been shown that there is an interaction between acetonitrile and methanol molecule ($k_{ass.}$ = 1.23) *via* hydrogen bonding in their binary mixtures[18].

The changes of log k_f of the (4′-nitrobenzo-15C5 Ni)$^{2+}$, (4′-nitrobenzo-15C5 Co)$^{2+}$ and (4′-nitrobenzo-15C5 Cu)$^{2+}$ complexes *vs.* the ionic radii in various AN-MeOH binary mixtures is shown in Fig. 3. Some reversals of stability can be observed which show that the selectivity order of the ligand for these metal cations is affected by the nature and composition of the solvent systems. As evident from Fig. 3, the order of selectivity of the metal-ion complexes in pure AN at 25 ºC is: $Co^{2+} > Cu^{2+} > Ni^{2+}$, but in pure MeOH is: $Ni^{2+} > Cu^{2+} > Co^{2+}$. It is interesting to note that the selectivity order of the complexes in binary mixtures of AN-MeOH with 25 and 50 mol % of AN is: $Ni^{2+} > Co^{2+} > Cu^{2+}$, but in the case of 75 mol % of AN, the selectivity sequence changes to: $Co^{2+} > Ni^{2+} > Cu^{2+}$. The results obtained in this study show that the selection of solvents as mixture components and their concentration may create possibilities to change the properties of the solvent system in a desired direction.

The changes of the thermodynamic parameter ($\Delta S°c$) of complexation of Ni^{2+}, Co^{2+} and Cu^{2+} metal cations by 4′-nitrobenzo-15C5 with the mole fraction of AN are shown in Fig. 4.
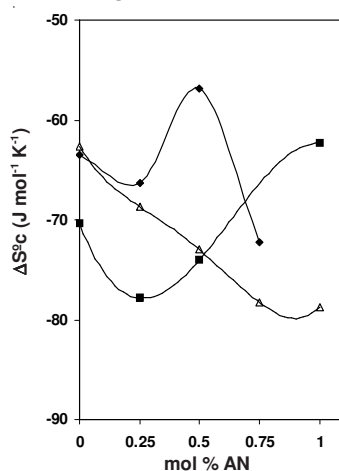

Fig. 4.   Changes of $\Delta S°c$ with the composition of the AN-MeOH binary systems at 25 ºC: (4′-nitrobenzo-15C5 Ni)$^{2+}$ ■, (4′-nitrobenzo-15C5 Co)$^{2+}$ **Δ**, (4′-nitro-benzo-15C5 Cu)$^{2+}$ ◆

As seen from Fig. 4, the changes of $\Delta S^o c$ is non-monotonically with the composition of the mixed solvents. This behaviour also seen for $\Delta H^o c$ which may reflect changes occurring in the structural distribution of solvent molecules in the solvent mixtures.

REFERENCES

1. C.J. Pedersen, *J. Am. Chem. Soc.*, **89**, 2495 (1967).
2. C.J. Pedersen, *J. Am. Chem. Soc.*, **92**, 391 (1970).
3. D.E. Fenton, *Chem. Soc. Rev.*, **6**, 325 (1977).
4. M.A. Rahman, N. Kwon, M. Won, M. Hyun and Y. Shim, *Anal. Chem.*, **76**, 3660 (2004).
5. S. Sawada, H. Torii, T. Osakai and T. Kimoto, *Anal. Chem.*, **70**, 4286 (1998).
6. M.A.F. Elmosallamy, *Anal. Chim. Acta*, **564**, 253 (2006).
7. V. Souchon, I. Leray and B. Valeur, *Chem. Commun.*, **40**, 4224 (2006).
8. N.B. Sankaran, S. Nishizawa, M. watanabe, T. Uchida and N. Teramae, *J. Mater. Chem.*, **15**, 2755 (2005).
9. J.M. Goodman and J.K.M. Sanders, *New J. Chem.*, **23**, 897 (1999).
10. M. Mazik, M. Kuschel and W. Sicking, *Org. Lett.*, **8**, 855 (2006).
11. M.J. Deetz, M. Shang and B.D. Smith, *J. Am. Chem. Soc.*, **122**, 6201 (2000).
12. D.J. Cram, T. Kaneda, R.C. Helgeson and G.M. Lein, *J. Am. Chem. Soc.*, **101**, 6752 (1979).
13. J.J. Christensen, D.J. Eatough, J. Rackman and R.M. Izatt, *Thermochim. Acta*, **3**, 219 (1972).
14. M. Shorprer and Z. Luz, *J. Am. Chem. Soc.*, **97**, 2805 (1975).
15. Genplot, Computer Graphic Service, USA (1989).
16. G.H. Rounaghi, Z. Eshaghi and E. Ghiamati, *Talanta*, **74**, 275 (1997).
17. N. Parasad, R. Singh, O. Prakash and S. Prakash, *Indian J. Pure Appl. Phys.*, **14**, 676 (1976).
18. G.A. Krestor and N.P. Novosyolov, in ed.: T.K. Kemp, Ionic Solvation, Ellis Harwood, New York (1994).