

Conductometric Study of Complexation Reaction of 4'-Nitrobenzo-15-crown-5 with Mn^{+2} , Co^{+2} , Y^{+3} , and ZrO^{+2} Cations in Acetonitrile, Methanol and Their Binary Solvent Solutions¹

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Received April 2, 2014

Abstract—The complexation reactions of Mn^{2+} , Co^{2+} , Y^{3+} , and ZrO^{2+} cations with the macrocyclic ligand, 4'-nitrobenzo-15-crown-5 (4'-NB15C5), in acetonitrile (AN), methanol and AN–MeOH binary mixtures have been studied at various temperatures using the conductometric method. The conductance data stand for the Me : L stoichiometric ratio 1 : 1. Values of the formation constants of the complexes were accumulated by plotting molar conductivity curves using the computer program, GENPLOT. The order of stability of the metal–ion complexes in pure AN at 15°C was found to be: $(4'-NB15C5 \cdot ZrO)^{2+} > (4'-NB15C5 \cdot Mn)^{2+} \approx (4'-NB15C5 \cdot Co)^{2+} > (4'-NB15C5 \cdot Y)^{3+}$. In the case of AN–MeOH binary solvent solutions with 50 and 75 mole percent of AN at the same temperature, the sequence of stability of the complexes was the following: $(4'-NB15C5 \cdot Mn)^{2+} > (4'-NB15C5 \cdot ZrO)^{2+} \approx (4'-NB15C5 \cdot Co)^{2+} > (4'-NB15C5 \cdot Y)^{3+}$, and $(4'-NB15C5 \cdot Mn)^{2+} > (4'-NB15C5 \cdot Co)^{2+} > (4'-NB15C5 \cdot ZrO)^{2+}$, respectively. The complexes formed are entropy stabilized in all cases.

Keywords: 4'-nitrobenzo-15-crown-5; Mn^{+2} ; Co^{+2} ; Y^{+3} ; ZrO^{+2} ; acetonitrile–methanol; conductometry

DOI: 10.1134/S1070363214060280

INTRODUCTION

The earliest crown ethers identified contained only oxygen donor atoms and sulfur, nitrogen-containing crown ethers were synthesized later. Due to differences in polarizability, nitrogen-containing crown ethers (azacrowns) and sulfur-containing crown ethers (thiacrowns) display different ionic selectivity from those of oxygen-containing analogues [1, 2]. Such difference in the character of O, N and S containing macrocyclic ligands can be explained in terms of the hard-soft acid-base theory [1, 2].

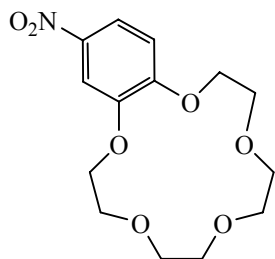
Macrocyclic polyethers like crown ethers are used both in chemistry and biology. These compounds act as anti-ulcer agents against histamine induced ulcers [3] and as antibacterial agents [4]. They are used in separation and transport processes in recovery or removal of metal cations from solutions [5–7], in ion-selective electrodes [8–10], recognition of isomers [11], as catalysts in phase transfer catalysis and in

medical diagnostic, and therapeutic agents [12, 13], for example, crown ether-substituted phthalocyanines (Pcs) in photodynamic therapy of cancer [14]).

The most important property of crown ethers is their complexation with various ionic, predominately cationic, species in solutions [15–17]. The factors that govern complexation and selectivity of crown ethers with metal cations [5, 18] are following: (a) the relative size of the cation and the crown cavity, (b) cation charge and type, (c) counter anion nature, (d) number and type of donor atoms, (e) substituents at the crown, (f) electron density of the crown cavity, (g) the crown ether ring flexibility, and (h) the effect of solvents.

Conductometry is a reliable instrumental method for determination of stability, selectivity and thermodynamic parameters of crown ether complexes with various metal cations in solutions [5]. It is also a highly sensitive and inexpensive technique with a simple experimental setting. The significant advantage of conductometry is its high precision even at very low solutions concentration [19].

¹ The text was submitted by the authors in English.



Scheme 1. Structure of 4'-nitrobenzo-15-crown-5.

The goal of the present study is determination of influence of nature and composition of the solvents (AN and MeOH and AN–MeOH) on selectivity and thermodynamics of the complexation reaction of 4'-nitrobenzo-15-crown-5 (Scheme 1) with Mn^{2+} , Co^{2+} , Y^{3+} , and ZrO^{2+} cations using the conductometric technique.

EXPERIMENTAL

Materials. High purity 4'-nitrobenzo-15-crown-5, manganese(II) chloride [$\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$], yttrium(III) nitrate [$\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$], cobalt(II) nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], methanol and acetonitrile (Merck Chemical Company) did not need further purification. Zirconium(IV) oxynitrate was from PROLABO.

Procedures. Determination of stability constants of complexes: 20 mL of a 10^{-4} M solution of metal salt was placed into a titration cell and the conductance of solution was measured, followed by steady increase in the crown ether concentration and rapid addition of the crown ether in the same solvent solution (2.0×10^{-3} M)

to the titration cell using a microburette. The conductance of the solution in the cell was measured after each transfer at the desired temperature. The conductance measurements were fulfilled using a digital JENWAY conductometer (Model 4510) in a water bath (LAUDA) temperature maintained at a certain level within the range $\pm 0.01^\circ\text{C}$. All experiments were performed under moderate stirring of the solutions. The same conductometric cell (cell constant of 0.98 cm^{-1}) was used throughout the study.

RESULTS AND DISCUSSION

The relationships of molar conductance (Λ_m) and the ratio $[\text{L}]_t/[\text{M}]_t$ for complexation of 4'-NB15C5 with Mn^{2+} , Co^{2+} , Y^{3+} , and ZrO^{2+} cations in pure acetonitrile and methanol and binary solvents were measured at different temperatures. $[\text{M}]_t$ is the total concentration of the cation and $[\text{L}]_t$ is the total concentration of the 4'-NB15C5.

The change of molar conductance values versus ligand/metal cation mole ratios for $(4'\text{-NB15C5} \cdot \text{Mn})^{2+}$ complex in AN–MeOH (AN 75 mol %) binary solvent solution at various temperatures is presented by Fig. 1. According to Fig. 1, addition of 4'-NB15C5 to Mn^{2+} cation solution in AN–MeOH binary system, resulted in increase of molar conductivity which indicates higher mobility of the $(4'\text{-NB15C5} \cdot \text{Mn})^{2+}$ complex compared to the free solvated Mn^{2+} cation. The slope of the molar conductivity curves (Fig. 1) changes smoothly, which emphasizes the formation of a

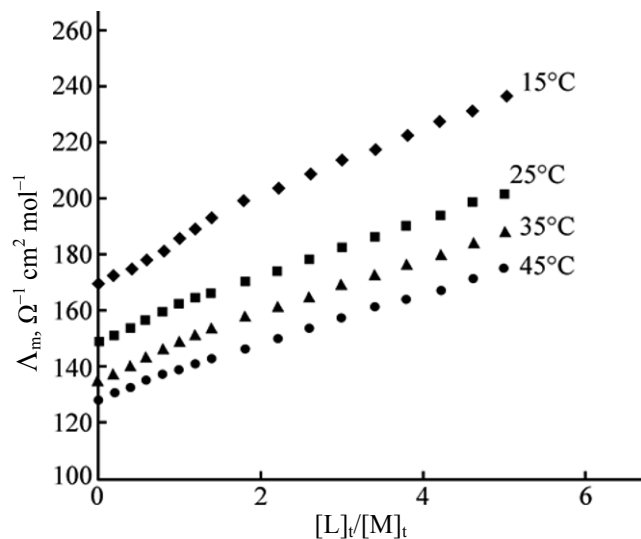


Fig. 1. Molar conductance-mole ratio plots for $(4'\text{-NB15C5} \cdot \text{Mn})^{2+}$ complex in AN–MeOH (AN, 75 mol %) at various temperature.

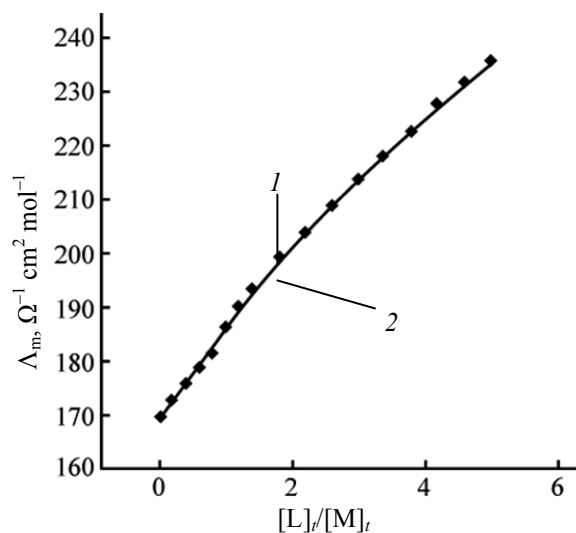


Fig. 2. Fitting and experimental curves for $(4'\text{-NB15C5} \cdot \text{Mn})^{2+}$ complex in AN–MeOH (AN, 75 mol %) binary solvent system at 15°C . (1) Experimental, (2) fitting.

Table 1. $\log K_f$ values for $(4'\text{-NB15C5}\cdot\text{Mn})^{2+}$, $(4'\text{-NB15C5}\cdot\text{Co})^{2+}$, $(4'\text{-NB15C5}\cdot\text{Y})^{3+}$, and $(4'\text{-NB15C5}\cdot\text{ZrO})^{2+}$ complexes in AN–MeOH binary mixtures at various temperature

Compound	$\log K_f \pm \text{SD}^a$			
	15°C	25°C	35°C	45°C
$(4'\text{-Nitrobenzo-15C5}\cdot\text{Mn})^{2+}$				
Pure AN	2.73 ± 0.12	2.75 ± 0.11	2.75 ± 0.14	2.75 ± 0.14
75.0% AN–25.0% MeOH	2.95 ± 0.05	2.74 ± 0.07	2.83 ± 0.05	2.81 ± 0.07
50.0% AN–50.0% MeOH	3.05 ± 0.09	2.81 ± 0.11	2.80 ± 0.05	2.79 ± 0.08
25.0% AN–75.0% MeOH	2.75 ± 0.12	2.69 ± 0.13	2.75 ± 0.10	2.75 ± 0.10
Pure MeOH	2.79 ± 0.09	2.73 ± 0.11	2.77 ± 0.09	2.74 ± 0.11
$(4'\text{-Nitrobenzo-15C5}\cdot\text{Co})^{2+}$				
Pure AN	2.73 ± 0.12	2.72 ± 0.15	2.72 ± 0.17	2.66 ± 0.13
75.0% AN–25.0% MeOH	2.81 ± 0.09	2.76 ± 0.14	2.70 ± 0.18	2.69 ± 0.13
50.0% AN–50.0% MeOH	2.79 ± 0.10	2.72 ± 0.14	2.79 ± 0.19	2.74 ± 0.19
25.0% AN–75.0% MeOH	2.79 ± 0.11	2.74 ± 0.12	2.76 ± 0.11	2.74 ± 0.12
Pure MeOH	2.83 ± 0.11	2.76 ± 0.09	2.72 ± 0.11	2.70 ± 0.13
$(4'\text{-Nitrobenzo-15C5Y})^{3+}$				
Pure AN	2.65 ± 0.09	2.77 ± 0.09	2.75 ± 0.11	2.76 ± 0.16
75.0% AN–25.0% MeOH	2.72 ± 0.12	2.74 ± 0.10	2.77 ± 0.09	2.71 ± 0.14
50.0% AN–50.0% MeOH	2.80 ± 0.07	2.73 ± 0.15	2.74 ± 0.10	2.74 ± 0.10
25.0% AN–75.0% MeOH	2.83 ± 0.07	2.70 ± 0.12	2.82 ± 0.10	2.69 ± 0.15
Pure MeOH	2.80 ± 0.08	2.70 ± 0.17	2.72 ± 0.17	2.71 ± 0.15
$(4'\text{-Nitrobenzo-15C5}\cdot\text{ZrO})^{2+}$				
Pure AN	2.81 ± 0.06	2.70 ± 0.17	2.85 ± 0.10	2.74 ± 0.15
75.0% AN–25.0% MeOH	2.79 ± 0.08	2.75 ± 0.10	2.84 ± 0.06	2.81 ± 0.09
50.0% AN–50.0% MeOH	2.73 ± 0.19	2.75 ± 0.10	2.72 ± 0.15	2.72 ± 0.12
25.0% AN–75.0% MeOH	2.78 ± 0.13	2.77 ± 0.09	2.77 ± 0.09	2.73 ± 0.11
Pure MeOH	2.75 ± 0.11	2.72 ± 0.12	2.74 ± 0.15	2.72 ± 0.16

^a (SD) standard deviation.

relatively weak complex between 4'-NB15C5 and Mn^{2+} cation in AN–MeOH binary solvent solution. Similar effect was observed with Y^{3+} , Co^{2+} and ZrO^{2+} cations in all solvents under study. The 1 : 1 [ML] complexation model is justified by fitting and experimental curves for $(4'\text{-NB15C5}\cdot\text{Mn})^{2+}$ complex in AN–MeOH (AN 75 mol %) binary solvent at 15°C (Fig. 2). Evidently there is a very good agreement between the fitting and experimental data. Hence our assumption of 1 : 1 stoichiometry for the complexation process is justified.

The stability constants of the complexes at each temperature were obtained from variation of molar conductance as a function of $[4'\text{-NB15C5}]_f/[M]_t$ molar ratio plots using the GENPLOT computer program [20]. Calculation of the stability constant of complexes

measured by conductometry is presented in the publication [21]. The values of $\log K_f$ for $(4'\text{-NB15C5}\cdot\text{M})^{n+}$ ($M^{n+} = \text{Mn}^{2+}$, Co^{2+} , Y^{3+} , and ZrO^{2+}) complexes in various solvent systems are listed in Table 1.

Changes in the stability constant ($\log K_f$) of $(4'\text{-NB15C5}\cdot\text{Mn})^{2+}$ complex versus the ratio of the components of the AN–MeOH binary solvent solution at various temperature is listed in Fig. 3. According to the latter, the stability constant ($\log K_f$) of the complex at 25, 35, and 45°C does not change within experimental error. Nevertheless, a non-linear relationship is observed between $\log K_f$ of $(4'\text{-NB15C5}\cdot\text{Mn})^{2+}$ complex and the composition of AN–MeOH binary solvent system at 15°C. This behavior may be due to changing the structure of the solvent system at this

Table 2. Thermodynamic parameters of $(4'\text{-NB15C5}\cdot\text{Mn})^{2+}$, $(4'\text{-NB15C5}\cdot\text{Co})^{2+}$, $(4'\text{-NB15C5}\cdot\text{Y})^{3+}$, and $(4'\text{-NB15C5}\cdot\text{ZrO})^{2+}$ complexes in AN–MeOH binary solvent solutions

Compound	$\log K_f \pm \text{SD}^a$ (25°C)	$-\Delta G_{s,298.15}^0 \pm \text{SD}$, kJ/mol	$\Delta H_s^0 \pm \text{SD}$, kJ/mol	$\Delta S_s^0 \pm \text{SD}$ kJ/mol
$(4'\text{-Nitrobenzo-15C5}\cdot\text{Mn})^{2+}$				
Pure AN	2.75 ± 0.11	15.67 ± 0.60	~ 0	52.56 ± 2.01
75.0% AN–25.0% MeOH	2.74 ± 0.07	15.63 ± 0.41	-7.88 ± 1.41	78.85 ± 4.52
50.0% AN–50.0% MeOH	2.81 ± 0.11	16.06 ± 0.63	~ 0	53.86 ± 2.11
25.0% AN–75.0% MeOH	2.69 ± 0.13	15.36 ± 0.75	~ 0	51.52 ± 2.51
Pure MeOH	2.73 ± 0.11	15.61 ± 0.60	~ 0	52.36 ± 2.01
$(4'\text{-Nitrobenzo-15C5}\cdot\text{Co})^{2+}$				
Pure AN	2.72 ± 0.15	15.52 ± 0.84	~ 0	63.19 ± 4.64
75.0% AN–25.0% MeOH	2.76 ± 0.14	15.75 ± 0.74	-7.38 ± 1.04	78.85 ± 4.52
50.0% AN–50.0% MeOH	2.72 ± 0.14	15.53 ± 0.81	~ 0	52.09 ± 2.71
25.0% AN–75.0% MeOH	2.74 ± 0.12	15.64 ± 0.69	~ 0	52.89 ± 2.31
Pure MeOH	2.76 ± 0.09	15.77 ± 0.52	-7.41 ± 1.34	77.74 ± 4.15
$(4'\text{-Nitrobenzo-15C5Y})^{3+}$				
Pure AN	2.77 ± 0.09	15.82 ± 0.52	~ 0	53.06 ± 1.74
75.0% AN–25.0% MeOH	2.74 ± 0.10	15.67 ± 0.57	~ 0	52.56 ± 1.91
50.0% AN–50.0% MeOH	2.73 ± 0.15	15.60 ± 0.88	~ 0	52.32 ± 2.95
25.0% AN–75.0% MeOH	2.70 ± 0.12	15.44 ± 0.71	~ 0	51.79 ± 2.38
Pure MeOH	2.70 ± 0.17	15.44 ± 0.97	~ 0	51.79 ± 3.25
$(4'\text{-Nitrobenzo-15C5}\cdot\text{ZrO})^{2+}$				
Pure AN	2.70 ± 0.17	15.44 ± 1.02	~ 0	51.79 ± 3.42
75.0% AN–25.0% MeOH	2.75 ± 0.10	15.71 ± 0.58	~ 0	52.69 ± 1.94
50.0% AN–50.0% MeOH	2.75 ± 0.10	15.71 ± 0.56	~ 0	52.69 ± 1.88
25.0% AN–75.0% MeOH	2.77 ± 0.09	15.79 ± 0.51	~ 0	52.95 ± 1.71
Pure MeOH	2.72 ± 0.12	15.54 ± 0.67	~ 0	52.12 ± 2.24

temperature and, therefore, changing the solvation number of the metal cation, ligand and even the resulting complex in solutions [22]. The hetero atom

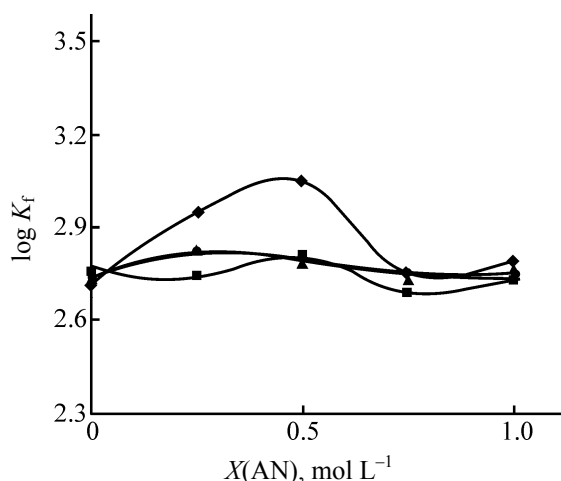


Fig. 3. Changes of the stability constant ($\log K_f$) of $(4'\text{-NB15C5}\cdot\text{Mn})^{2+}$ complex related to the ratio of AN–MeOH binary system at various temperature.

selective solvation and formation of the mixed solvates in solutions may also influence upon the effect.

The order of stability of the metal–ion complexes in pure AN at 15°C was determined as follows: $(4'\text{-NB15C5}\cdot\text{ZrO})^{2+} > (4'\text{-NB15C5}\cdot\text{Mn})^{2+} \approx (4'\text{-NB15C5}\cdot\text{Co})^{2+} > (4'\text{-NB15C5}\cdot\text{Y})^{3+}$. But in the case of the binary mixtures of AN–MeOH (AN mol % = 50 and 75) at the same temperature, the sequence of stability of the complexes varies as: $(4'\text{-NB15C5}\cdot\text{Mn})^{2+} > (4'\text{-NB15C5}\cdot\text{ZrO})^{2+} \approx (4'\text{-NB15C5}\cdot\text{Co})^{2+} > (4'\text{-NB15C5}\cdot\text{Y})^{3+}$ and $(4'\text{-NB15C5}\cdot\text{Mn})^{2+} > (4'\text{-NB15C5}\cdot\text{Y})^{3+} \approx (4'\text{-NB15C5}\cdot\text{Co})^{2+} > (4'\text{-NB15C5}\cdot\text{ZrO})^{2+}$, respectively.

According to the data accumulated in the current study, the selectivity of the ligand towards the metal cations in solutions is solvent dependent.

The Gibbs standard free energy (ΔG_s^0) of the complexation reactions of 4'-NB15C5 with the studied cations, was deduced from thermodynamic equilibrium constants of the complexes. The changes in the

Table 3. log K_f values for the 4'-NB15C5 and B15C5 complexes with Mn^{2+} cation in AN solution at various temperature

Complex	45°C	35°C	25°C	15°C	References
$(4'\text{-NB15C5} \cdot \text{Mn})^{2+}$	2.73±0.12	2.75±0.11	2.75±0.14	2.75±0.14	This work
$(\text{B15C5} \cdot \text{Mn})^{2+}$	5.30±0.30	4.78±0.30	4.46±0.12	4.53±0.15	[23]

standard enthalpy (ΔH_s^0) for the complexation reaction were derived from the slope of the van't Hoff plots, and the changes in standard entropy (ΔS_s^0) were calculated in accordance with the relationship $\Delta G_{s,298.15}^0 = \Delta H_s^0 - 298.15\Delta S_s^0$. The values of the standard thermodynamic data that are summarized in Table 2, demonstrate that in all solvent systems the complexes formed between the ligand and Mn^{2+} , Co^{2+} , Y^{3+} , and ZrO^{2+} cations are entropy stabilized. According to data listed in Table 1, in most cases, the stability constants of the complexes are not temperature dependant. The changes in ΔH_s^0 are negligible. Hence, the complexation processes between 4'-NB15C5 and the studied cations are athermic in the title solvents.

The data accumulated in the study of the complexation reaction of benzo15-crown-5 [23] and 4'-nitrobenzo15-crown-5 with Mn^{2+} cation in acetonitrile solutions at different temperatures, are listed in Table 3. Comparison of these results reveals that the complex formation constant (log K_f) of $(4'\text{-NB15C5} \cdot \text{Mn})^{2+}$ complex at various temperatures, is lower than that of $(\text{B15C5} \cdot \text{Mn})^{2+}$ complex. It had been determined that interaction between cations and the ether compounds, depends on the basicity of the ether oxygen atoms. It is probable that the electron acceptor effect of both the nitro and benzo groups in the 4'-NB15C5 molecules diminishes the basicity of two oxygen atoms in the poly ether ring and, therefore, the stability constant of the $(4'\text{-NB15C5} \cdot \text{Mn})^{2+}$ complex is lowered due to the presence of the nitrobenzo fragment in this macrocyclic ligand. Probably introduction of the chosen substitutions in the structure of the crown ether molecules, results in a significant change in the binding energy of the crown ether complexes which could be an effective factor for controlling the selectivity of the crown ethers towards metal cations in solutions.

ACKNOWLEDGMENTS

The authors acknowledge the support of this research work by Ferdowsi University of Mashhad, Mashhad, Iran.

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