Complexation Study of *N*-Phenylaza-15-Crown-5 with Cd²⁺ Cation in Binary Mixed Non-aqueous Solvents

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The complexation reaction of *N*-phenylaza-15-crown-5 (PhA15C5) with Cd²⁺ cation was studied in acetonitrile-methanol, acetonitrile-butanol, acetonitrile-ethylacetate, acetonitrile-nitromethane and methanol-propylencarbonate binary solvent solutions, at different temperatures by conductometric method. The stability constant of the resulting 1:1 complex at each temperature was determined using a computer fitting conductance-mole ratio data. A non-linear relationship was observed for changes of log K_f of (PhA15C5.Cd)²⁺ complex *versus* the composition of the binary mixed solvents. The corresponding standard thermodynamic parameters ($\Delta H°_c$, $\Delta S°_c$) were obtained from temperature dependence of the stability constant. The results show that the complexation reaction is enthalpy destabilized but entropy stabilized.

Key Words: *N*-Phenylaza-15-crown-5, Cd²⁺ cation, Mixed non-aqueous solvents, Conductometry.

INTRODUCTION

Cadmium is a highly toxic metal and is known as a significant environmental pollutant with a wide variety of adverse effects. Occupational exposure to cadmium has long been known to be harmful to the kidney, lung and liver[1,2]. Many organic compounds, including crown ethers, play an important role in complexing the cadmium(II) cation and are important determinants of the environmental fate and transport of this metal cation[3,4].

Among several factors influencing the formation of macrocyclic complexes, the ability of solvent molecules to solvate metal ions and, thus, to compete with the donating groups of the ligands for the coordination sites of the central cation plays a fundamental role[5]. Perhaps equally important, but often neglected, is the interaction of some solvents molecules with macrocyclic ligands[6-8]. Since both the cation and the macrocycle must be at least partially desolvated before the complex can be formed, the two solvation processes are expected to markedly influence the overall stability of the resulting complex in solution.

There has recently been increasing interest in the study of complexation reactions in binary mixed solvent systems[9-12]. The study of complexation reactions of crown ethers in non-aqueous matrices could be used as an efficient strategy to design the analytical systems such as, potentiometric sensors, bulk liquid membrane transport, optical sensors, solid phase extraction and biochemistry fields.

Studies of crown ethers complexation in different solvents show that the thermodynamic and kinetic parameters are affected by the nature and the composition of the solvent system[13-16]. Thermodynamic studies of macrocyclic complexation reactions with metal cations not only provide relevant information on the binding process, but also lead to a better understanding of the selective behaviour of these ligands toward different metal cations.

In the present investigate, we report the results of thermodynamic study for complexation reaction between *N*-phenylaza-15-crown-5 (**Scheme-I**) with Cd²⁺ cation in acetonitrile-methanol (AN-MeOH), acetonitrile-butanol (AN-BuOH), acetonitrile-nitromethane (AN-NM) acetonitrile-ethylacetate (AN-EtOAc) and methanol-propylencarbonate (MeOH-PC) binary solutions at different temperatures using the conductometric method.
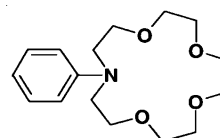
Scheme-I: Structure of *N*-phenylaza-15-crown-5

EXPERIMENTAL

N-Phenylaza-15-crown-5 (PhA15C5) and Cd(NO₃)₂ with the highest purity were purchased from Merck and were used without any further purification except for vacuum drying. The

organic solvents (all from Merck) were used without further purification. Conductance measurements were performed using a digital Metrohm conductometer (model 712) in a water bath thermostated at a constant temperature which maintained within ± 0.01 ºC. The electrolytic conductance was measured using a cell consisting of two platinum electrodes to which an alternating potential was applied. The calibration of conducto-metric cell was made with the use of an aqueous KCl solution and the cell constant was found to be of 0.73 cm^{-1}.

Procedure: The experimental procedure to obtain the stability constant of (PhA15C5.Cd)$^{2+}$ complex was as follows: a solution of metal salt (1.0×10^{-4} mol L^{-1}) 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} mol L^{-1}) 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.

RESULTS AND DISCUSSION

Conductance studies: In order to study the influence of adding PhA15C5 on the molar conductance of Cd^{2+} cation in AN-MeOH, AN-BuOH, AN-EtOAc, AN-NM and MeOH-PC binary solutions, the conductivity of the solutions at a constant salt concentration (1.0×10^{-4} mol L^{-1}) was monitored while increasing the macrocycle concentration at various tempe-ratures. The molar conductance *versus* ligand/cation mole ratio plots for (PhA15C5.Cd)$^{2+}$ complex in AN-MeOH (mol % AN=25) binary solvent solution at different temperatures are shown in Fig. 1. As is seen from this figure, addition of PhA15C5 to Cd^{2+} cation at different temperatures shows an increase in molar conductivity, which indicates that the (PhA15C5.Cd)$^{2+}$ complex in this solvent is more mobile than free solvated Cd^{2+} cation. Similar behaviour was observed in all other studied systems.
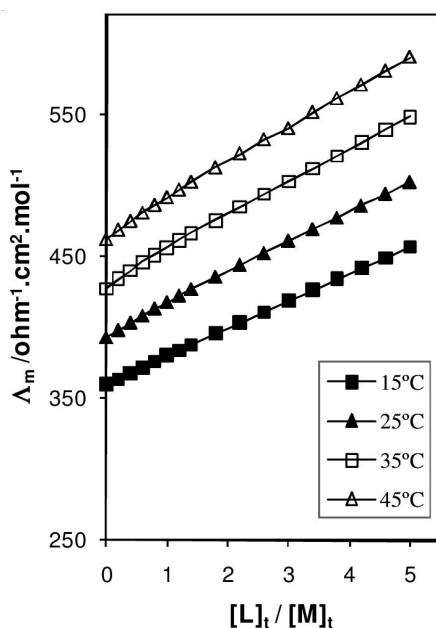

Fig. 1. Molar conductance-mole ratio plots for (PhA15C5.Cd)$^{2+}$ complex in AN-MeOH (mol % AN = 25) binary solvent system at different temperatures

In all cases, the corresponding molar conductivity *versus* [L]$_t$/[M]$_t$ plots does not show a considerable change in their slopes at a mole ratio of about 1, emphasizing the formation of weak 1:1 complex between PhA15C5 and Cd^{2+} cation. Moreover, the entire resulting molar conductance-mole ratio data were fitted by [M:L] program, which further supports the formation of 1:1 (ligand to metal ion) complex in solutions.

In order to make more clear the 1:1 [M:L] complexation model, the fitting and experimental curves for (PhA15C5.Cd)$^{2+}$ complex in AN-MeOH (mol % AN = 25) binary solvent system at 25 ºC are shown in Fig. 2. As is evident in this figure, there is a very good agreement between the fitting and experimental data.
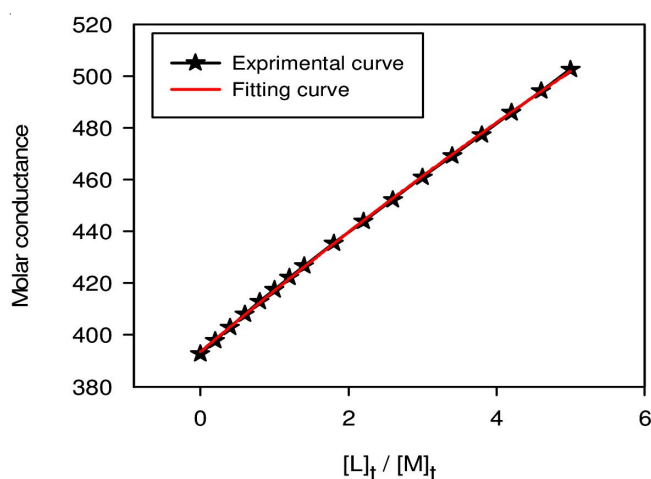

Fig. 2. Fitting and experimental curves for (PhA15C5.Cd)$^{2+}$ complex in AN-MeOH (mol % AN = 25) binary solvent system at 25 ºC

The stability constant of (PhA15C5.Cd)$^{2+}$ complex at each temperature was obtained from variation of molar conduc-tance as a function of [L]$_t$/[M]$_t$ molar ratios using a GENPLOT computer program[17]. The details of calculation of the stability constants of complexes by the conductometric method have been described elsewhere[9,11]. The values of the stability cons-tant (log K$_f$) for (PhA15C5.Cd)$^{2+}$ complex in various solvent systems are listed in Table-1. It should be noted that, in the process of calculation of formation constant of the complex, due to the highly dilute experimental conditions used in this study, it was assumed that the association of Cd^{2+} cation and NO$_3^-$ anion into ion-pair is negligible.

Effect of solvent composition: As is seen from Fig. 3, the change of the stability constant (logK$_f$) of (PhA15C5.Cd)$^{2+}$ complex with the composition of AN-MeOH binary system is not linear. A non-linear behaviour was also observed for other binary solutions. This behaviour may be due to the interactions between the methanol and acetonitrile molecules *via* hydrogen bonding in their binary mixtures, which results in changing the structure and properties of the mixed solvents and, there-fore, changing the solvation of the cation, the ligand and the resulting complex in these binary solvent solutions.

The preferential solvation of Cd^{2+} cation, the ligand, the resulting complex and even the counter ion and the charac-teristics of its changes with the composition of the mixed solvents may be another reason for this kind of behaviour. In mixed solvents, the energetic effect of the preferential solvation

depends quantitatively on the structural and energetic properties of the mixtures[18]. In addition, the non-monotonic behaviour observed for changes of $\log K_f$ of (PhA15C5.Cd)[2+] complex with the composition of the mixed solvents, probably reflects a balance between the solvation properties, donicity, hydrogen bonding ability, *etc*. of the solvent systems.

standard entropies were calculated from relationship: $\Delta G^{\circ}_{c, 298.15} = \Delta H^{\circ}_c - 298.15 \Delta S^{\circ}_c$. The results are summarized in Table-2.
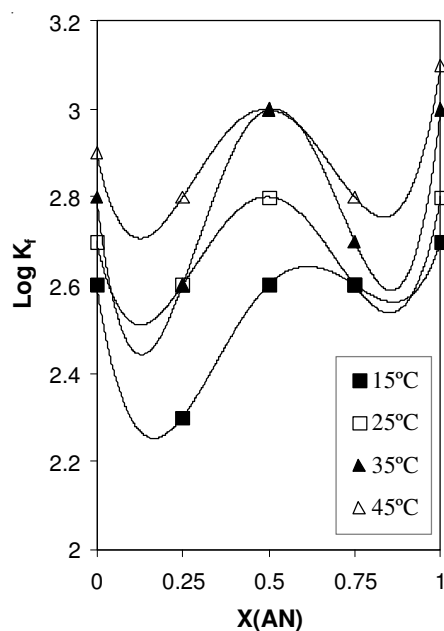

Fig. 3.　Changes of the stability constant ($\log K_f$) of (PhA15C5.Cd)[2+] complex with the composition of AN-MeOH binary system at different temperatures
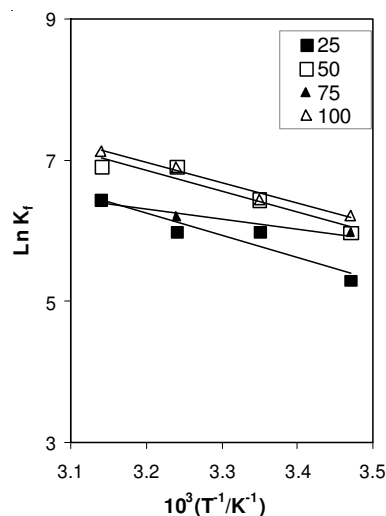
TABLE-1
log K_f VALUES OF (PhA15C5.Cd)[2+] COMPLEX IN AN–MeOH, AN–BuOH, AN– NM, AN– EtOAc AND MeOH – PC BINARY MIXTURES AT DIFFERENT TEMPERATURES

Medium	log k_f ± SD[a]			
	15 °C	25 °C	35 °C	45 °C
AN–MeOH				
Pure AN	2.7 ± 0.1	2.8 ± 0.1	3.0 ± 0.1	3.1 ± 0.1
75% AN–25% MeOH[b]	2.6 ± 0.1	2.6 ± 0.1	2.7 ± 0.1	2.8 ± 0.1
50% AN–50% MeOH	2.6 ± 0.1	2.8 ± 0.1	3.0 ± 0.1	3.0 ± 0.1
25% AN–75% MeOH	2.3 ± 0.1	2.6 ± 0.1	2.6 ± 0.1	2.8 ± 0.1
Pure MeOH	2.6 ± 0.1	2.7 ± 0.1	2.8 ± 0.1	2.9 ± 0.1
AN–BuOH				
Pure AN	2.7 ± 0.1	2.8 ± 0.1	3.0 ± 0.1	3.1 ± 0.1
75% AN–25% BuOH[b]	2.6 ± 0.2	2.6 ± 0.1	2.7 ± 0.2	2.8 ± 0.1
50% AN–50% BuOH	2.5 ± 0.2	2.6 ± 0.1	2.8 ± 0.1	2.8 ± 0.1
25% AN–75% BuOH	2.6 ± 0.2	2.7 ± 0.1	2.8 ± 0.1	c
Pure BuOH	2.8 ± 0.2	2.9 ± 0.1	2.9 ± 0.2	c
AN– NM				
Pure AN	2.7 ± 0.1	2.8 ± 0.1	3.0 ± 0.1	3.1 ± 0.1
75% AN–25% NM[b]	2.7 ± 0.1	2.8 ± 0.1	3.0 ± 0.1	3.1 ± 0.1
50% AN–50% NM	2.6 ± 0.1	2.7 ± 0.1	2.8 ± 0.1	2.9 ± 0.1
25% AN–75% NM	2.7 ± 0.2	2.8 ± 0.2	2.8 ± 0.1	2.9 ± 0.1
Pure NM	d	d	d	d
AN–EtOAc				
Pure AN	2.7 ± 0.1	2.8 ± 0.1	3.0 ± 0.1	3.1 ± 0.1
75% AN–25% EtOAc[b]	2.9 ± 0.1	3.0 ± 0.1	3.1 ± 0.1	3.1 ± 0.2
50% AN–50% EtOAc	2.5 ± 0.2	2.8 ± 0.2	3.0 ± 0.1	3.0 ± 0.2
25% AN–75% EtOAc	2.6 ± 0.2	2.7 ± 0.1	2.7 ± 0.1	2.8 ± 0.1
Pure EtOAc	d	d	d	d
MeOH–PC				
Pure MeOH	2.6 ± 0.1	2.7 ± 0.1	2.8 ± 0.1	2.9 ± 0.1
75% MeOH–25% PC[b]	2.5 ± 0.1	2.6 ± 0.1	2.7 ± 0.2	2.7± 0.2
50% MeOH–50% PC	2.6 ± 0.2	2.7 ± 0.1	2.7 ± 0.1	2.7 ± 0.2
25% MeOH–75% PC	2.6 ± 0.2	2.7 ± 0.1	2.7 ± 0.1	2.7 ± 0.2
Pure PC	2.6 ± 0.1	2.6 ± 0.1	2.8 ± 0.1	2.8 ± 0.1

[a]SD = standard deviation; [b]Composition of binary mixtures is expressed in mol % for each solvent system; [c]The data can not be fitted in equation; [d] The salt is not dissolved.

Fig. 4.　Van't Hoff plots for (PhA15C5.Cd)[2+] complex in different binary mixed solvents

Thermodynamic calculations: In order to have a better understanding of thermodynamics of complexation reactions of the metal cations with the ligands, it is useful to determine the contribution of enthalpy and entropy of the reactions. The ΔH°_c and ΔS°_c values for complexation process between PhA15C5 and Cd^{2+} cation were determined from the temperature dependence of the stability constant of (PhA15C5.Cd)[2+] complex using the van't Hoff plots. In all cases, the plots of $\ln K_f$ *vs.* 1/T were linear and a typical example of these plots for (PhA15C5.Cd)[2+] complex is shown in Fig. 4.

The values of standard enthalpies for complexation reaction were determined in the usual manner from the slope of the van't Hoff plots assuming that ΔC_p is equal to zero over the entire temperature range investigated. The values of the

The thermodynamic data given in Table-2, reveal that in all cases, the sign of the enthalpy values for formation of (PhA15C5.Cd)[2+] complex is positive and, therefore, the complexation process is endothermic (unfavorable). In all cases, the positive values of ΔS°_c characterize the formation of this complex. Hence, the (PhA15C5.Cd)[2+] complex is stabilized from entropy viewpoint. The two main factors, which affect the ΔS°_c values, are (i) the loss of conformational entropy of ligand upon complexation and (ii) the randomness of the solvent molecules in bulk solvent after being released during desolvation of metal cation and the ligand. It has been reasonably assumed that the positive entropy changes upon complexation are related to the release of some solvent molecules after desolvation process of the cation and the ligand[19,20].

TABLE-2
THERMODYNAMIC PARAMETERS FOR (PhA15C5.Cd)$^{2+}$
COMPLEX IN AN–MeOH, AN–BuOH, AN–NM, AN–EtOAc
AND MeOH–PC BINARY MIXTURES

Medium	$\Delta G^\circ_c \pm SD^a$ (kJ mol^{-1})	$\Delta H^\circ_c \pm SD^a$ (J mol^{-1})	$\Delta S^\circ_c \pm SD^a$ (J mol^{-1} K^{-1})
AN–MeOH			
Pure AN	-34.1 ± 0.6	18 ± 1	115.0 ± 5
75% AN–25% MeOH [b]	-30.7 ± 0.7	16 ± 3	103 ± 28
50% AN–50% MeOH	-40.7 ± 0.7	25 ± 9	137 ± 31
25% AN–75% MeOH	-30.8 ± 0.7	17 ± 7	104 ± 25
Pure MeOH	-37.5 ± 0.7	22 ± 3	126 ± 13
AN–BuOH			
Pure AN	-34.1 ± 0.6	18 ± 1	115.0 ± 5
75% AN–25% BuOH [b]	-25.6 ± 0.8	11 ± 2	86 ± 9
50% AN–50% BuOH	-32.4 ± 0.7	19 ± 4	109 ± 15
25% AN–75% BuOH	-30.4 ± 0.7	15 ± 8	102 ± 2
Pure BuOH	-29.4 ± 0.9	12± 6	94 ± 20
AN–NM			
Pure AN	-34.1 ± 0.6	18 ± 1	115.0 ± 5
75% AN–25% NM [b]	-27.2 ± 0.8	12 ± 2	91 ± 9
50% AN–50% NM	-28.4 ± 0.7	13 ± 3	95 ± 12
25% AN–75% NM	-40.0 ± 1	24 ± 3	135 ± 12
AN–EtOAc			
Pure AN	-34.1 ± 0.6	18 ± 1	115.0 ± 5
75% AN–25% EtOAc [b]	-24.4 ± 0.8	9 ± 1	82 ± 6
50% AN–50% EtOAc	-35.6 ± 1.0	20 ± 5	120 ± 17
25% AN–75% EtOAc	-27.8 ± 0.7	11 ± 2	93 ± 8
MeOH–PC			
Pure MeOH	-37.5 ± 0.7	22 ± 3	126 ± 13
75% MeOH–25% PC [b]	-26.6 ± 0.7	12 ± 6	89 ± 21
50% MeOH–50% PC	-23.9 ± 0.5	9 ± 3	80 ± 11
25% MeOH–75% PC	-30.5 ± 0.7	15 ± 5	101 ± 18
Pure PC	-27.2 ± 0.9	12 ± 4	91± 15

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

As is obvious from Table-2, the standard thermodynamic quantities (ΔH°_c, ΔS°_c) are quite sensitive to the nature and composition of the mixed solvents and a non-monotonic behaviour is observed between these thermodynamic functions and the composition of the binary solutions. This behaviour is due to the variations in the extent of the contribution of such important parameters as solvation-desolvation of the species involved in the complexation reaction (*i.e.*, cation, macrocycle and the resulting complex) and also the conformational changes of the macrocyclic ligand with the composition of solutions. Therefore, we should not expect a monotonic relationship between these thermodynamic quantities and the solvent composition. Similar behaviours have already been reported for various metal cation-crown ether complexes in different binary mixed solvents[11-13,18,21].

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