Conductometric Studies of the Thermodynamics of Complexation of Zn^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Mn^{2+}, Cu^{2+} Ions with 1,13-Bis(8-Quinolyl)-1,4,7,10,13-Pentaoxatridecane in Binary Solvent Mixtures

Payehghadr, Mahmood*[+]; Taghdiri, Mehdi; Zamani, Akram; Hesaraki, Neda
Department of Chemistry, Payame Noor University, PO BOX 19395-3697 Tehran, I.R. IRAN

ABSTRACT: *The complexation reaction between 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (Kryptofix5) ligand with Zn^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Mn^{2+} and Cu^{2+} ions were studied conductometrically in different AcetoNitrile-NitroMethane (AN-NM) and AcetoNitrile-Methanol (AN-MeOH) mixtures. The formation constants of the resulting 1:1 complexes were calculated from the computer fitting of the molar conductance in various mole ratios. The enthalpy and entropy changes of the complexation reactions were derived from conductometric titrations in different AN-NM mixtures at various temperatures. The results revealed that Kryptofix5 forms very stable 1:1 complexes with mentioned cations in all AN-NM and AN-MeOH mixtures. It was found that the stability of the resulting complexes decreased with increasing nitromethane or methanol in the solvent mixture. The $T\Delta S°$ vs. $\Delta H°$ plot of all thermodynamic data obtained shows a fairly good linear correlation indicating the existence of enthalpy-entropy compensation in the complexation reactions.*

KEY WORDS: *Conductometry, Stability constant, 1,13–Bis(8-quinolyl)-1,4,7,10,13- pentaoxatridecane, Kryptofix5, Complexation.*

INTRODUCTION

Since the first report of *Moore* and *Pressman* on the induction of the transport of potassium ions through the mitochondrial membrane by the antibiotic valinomycin [1], a series of other naturally occurring and synthetic compounds (including crown ethers and cryptands) has been discussed as potential ion carriers in artificial and biological membranes. Due to the similarities of open-chain polyethylene glycols in many respects to synthetic and naturally occurring antibiotics, there has been a growing interest in the coordination chemistry of these ligands and their metal ion complexes. However, in comparison with the macrocyclic crown ether and cryptands, much less thermodynamic data is available on the complexation of open chain polyethylene glycols.

Voegtle et al. investigated the complexation of Kryptofix5 (Fig. 1) and another open-chain quinoline polyether with alkali metal ions in methanol by absorption measurements [2] and then reported thermodynamic parameters of complexation for Kryptofix5 and alkali metal cations in methanol at 25ºC [3]. Competitive

** To whom correspondence should be addressed.*
+ E-mail: mpayehghadr@pnu.ac.ir , mahmood_payehghadr@yahoo.com
1021-9986/12/3/ 7/$/2.70

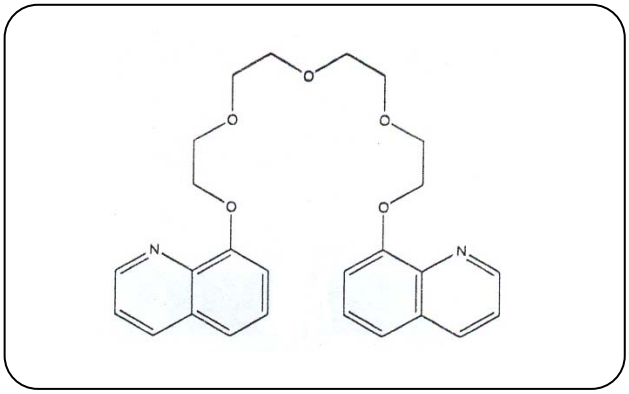

Fig. 1: The structure of Kryptofix5 ligand.

spectrophotometric method for the complexation studies of alkali, alkaline earth and transition metal ions with Kryptofix5 have been reported [4].

Recently the interaction of Kryptofix5 with alkali metal cations (Li^+, Na^+ and K^+) in aprotic medium (acetonitrile) has been investigated by conductometry and NMR methods [5].

It was of interest to us to study the interaction of transition and heavy metal ions with this ligand because it has been less reported in the literature particularly in binary mixed solvents. In the previous study, we reported our results of the complexation study between Kryptofix5 with Zn^{2+}, Ni^{2+}, Co^{2+}, $Pb^{2+}$and Cu^{2+} cations in acetonitrile by conductometry and spectrophotometry methods [6]. In order to further investigation of the solvent role, in the present study, we report our results of the same complexation reactions in binary solvent mixtures by conductometry.

EXPERIMENTAL SECTION

Reagents

Reagent grade Kryptofix5, Methanol (MeOH) and nitrate salts of cobalt, copper, zinc, nickel, manganese and lead (all from Merck), were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. Spectroscopic grade acetonitrile (Merck) was purified and dried by the previously described method [7]. The conductivity of the solvent was less than 1×10^{-7} S cm^{-1}. Reagent grade NitroMethane (NM) (Merck) was dried over magnesium sulfate and then distilled three times. The conductivity of the product was less than 5.0×10^{-7} S Cm^{-1} at 25°C. All the AN-NM and AN-MeOH mixtures were prepared by weight.

Conductometric titration

Conductometric measurements were carried out by Metrohm 712 conductometer equipped with a Haake D1 circulator. In a typical experiment, 10.0 mL of metal ion solution (5.0×10^{-5} $mol.L^{-1}$) in the solvent was placed in the titration cell, thermostated to the desired temperature and the conductance of solution was measured. Then, a known amount of concentrated solution of Kryptofix5 ligand in the same solvent (5×10^{-3} $mol.L^{-1}$) was added in a stepwise manner using a Hamilton syringe. The conductance of the solution was measured after each addition. The Kryptofix5 ligand solution was continually added until the desired ligand to cation mole ratio was achieved. In all measurements, cell was thermostated at desired temperature ±0.1ºC. The cell constant at the different temperature used was determined by measuring the conductivity of 1×10^{-2} $mol.L^{-1}$ solution of analytical grade KCl in triply distilled deionized water. The specific conductances of this solution at various temperatures have been reported in the literature [8]. A dip-type conductivity cell made of platinum black was used and the corresponding cell constant at 15, 25, 35 and 45ºC were 0.834, 0.832, 0.829 and 0.820 cm^{-1}, respectively.

The formation constants, K_f , of the resulting 1:1 complexes were calculated by fitting the observed molar conductance (Λ_{obs}) data at various [ligand]/[M^{2+}] mole ratios according to the method described in our previous publication [6].

RESULTS AND DISCUSSION

In order to evaluate the influence of adding Kryptofix5 on the molar conductance of Zn^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Mn^{2+} and Cu^{2+} ions in different AN-NM mixtures, the molar conductance at a constant metallic salt concentration (5.0×10^{-5} M) was monitored while increasing the Kryptofix5 concentration at various temperatures. The molar conductances vs. Kryptofix5/cation mole ratio plots were obtained and some of plots are shown in Figs. 2 and 3.

In order to investigate the role of the solvent, complexation reactions were also performed in pure MeOH and AN-MeOH mixtures at 25°C. Some of the resulting molar conductances vs. Kryptofix5/cation mole ratio plots are shown in Fig. 4.

Mole ratio plots indicate that in all cases, there is a gradual increase in the molar conductance with

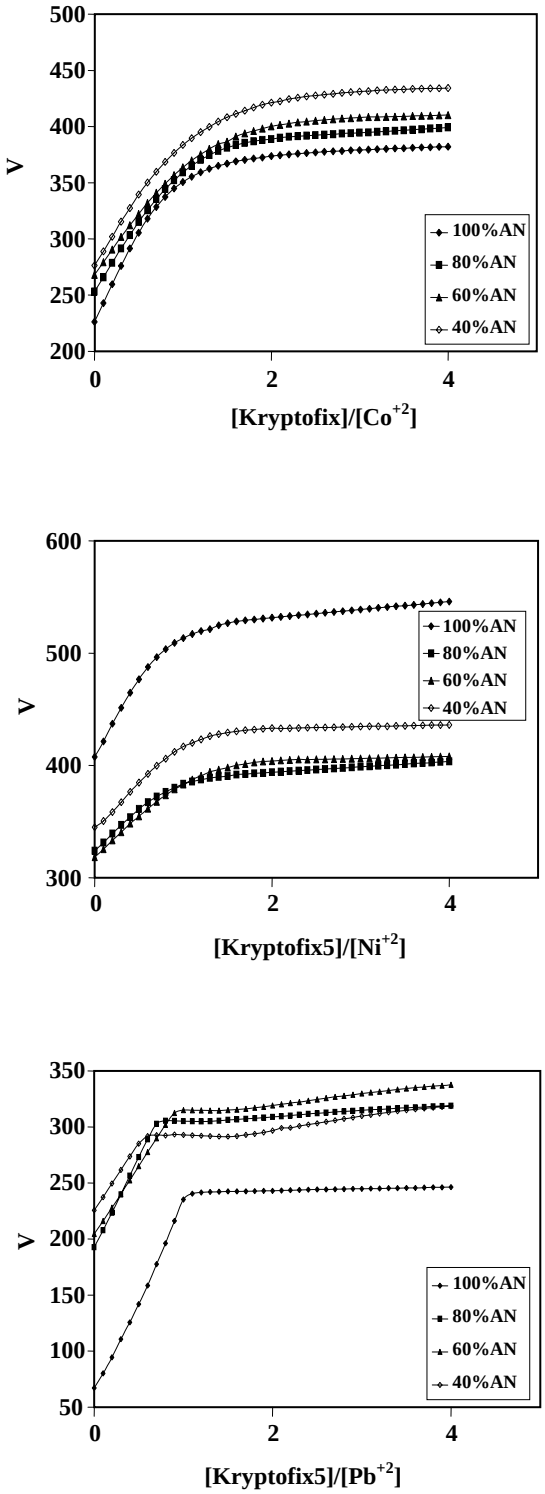

Fig. 2: Molar conductance (S cm^2 mol^{-1}) vs. [Kryptofix5]/[M^{2+}] for various Kryptofix5-M^{2+} systems at 25℃ in different AN-NM mixtures. The M^{2+} cations are (A) Co^{2+}, (B) Ni^{2+}, (C) Pb^{2+}.

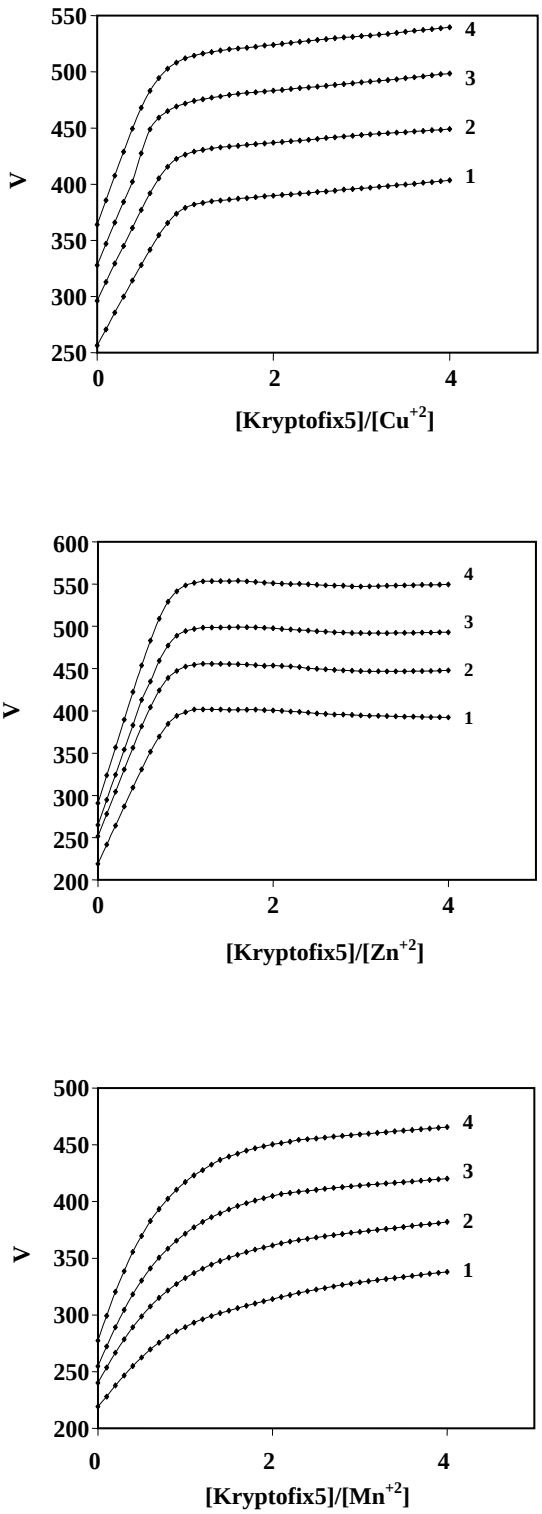

Fig. 3: Molar conductance (S cm^2 mol^{-1}) vs. [Kryptofix5]/[M^{2+}] plots in 40% AN-60% NM mixture at various temperatures: (1) 15℃, (2) 25℃, (3) 35℃, (4) 45℃. The M^{2+} cations are (A) Cu^{2+}, (B) Zn^{2+}, (C) Mn^{2+}.

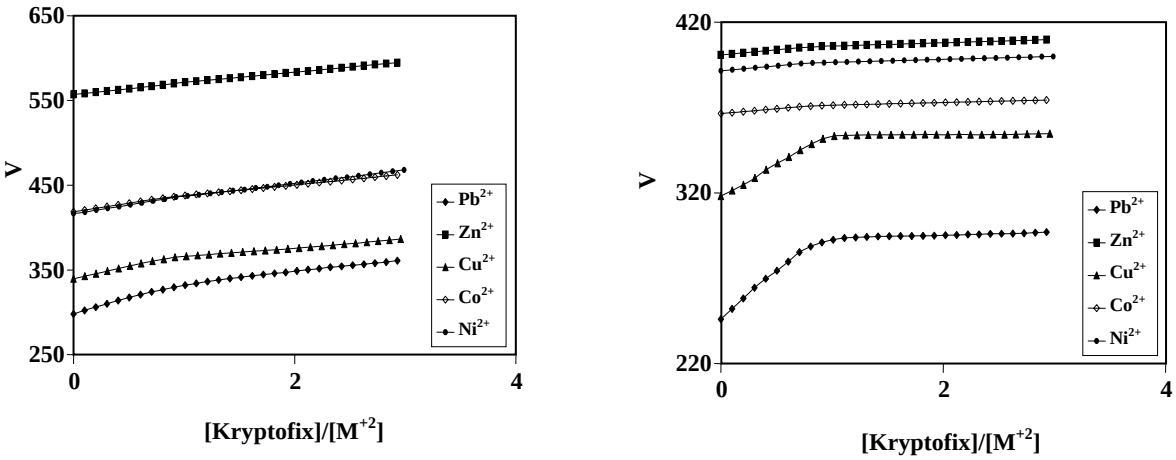

Fig. 4: Molar conductance (S cm^2 mol^{-1}) vs. [Kryptofix5]/[M^{2+}] for various Kryptofix5-M^{2+} systems at 25°C in (A) pure MeOH and (B) 40% AN-60% MeOH mixture.

an increase in the Kryptofix5 concentration. This could be due to the lower mobility of the solvated cation and existence of some ion pairing in the initial salt [9-11]. This might indicate that the complexes formed are more mobile than the solvated metals ions. From mole ratio plots of molar conductance vs. Kryptofix5/cation mole ratio it is seen that, in the all cases, the slopes of the corresponding molar conductance-mole ratio plots change sharply at the point, where the ligand to cation mole ratio is one, emphasizing the formation of stable 1:1 complexes between the ligand and the cations. Such a conductance behavior is indicative of the formation of ML complexes in solutions.

The formation constants of all Kryptofix5-M^{2+} complexes in AN-NM at various temperatures and in AN-MeOH at 25°C, obtained by computer fitting of the molar conductance-mole ratio data, are listed in Tables 1 and 2.

A sample computer fit of the mole ratio data is shown in Fig. 5. Our assumption of 1:1 stochiometry seems reasonable in the light of the fair agreement between the observed and calculated molar conductance. It should be noted that, in the procedure of calculation of formation constants, under the highly dilute experimental conditions (5×10^{-5} mol.L^{-1}), the association between M^{2+} and NO_3^- ion was considered negligible.

The data given in Tables 1 and 2 clearly illustrate the fundamental role of the solvent properties in the M^{2+}-Kryptofix5 complexation reactions studied.

In order to have a better understanding of the thermodynamics of complexation reactions of ions with Kryptofix5, it is useful to investigate the enthalpic and entropic contributions to these reactions. The ΔH° and ΔS°of the complexation reactions in different AN-NM mixtures were evaluated from the temperature dependence of the formation constants by applying a linear least-square analysis according to the Van't Hoff equation based on the method described in our previous publication [6].

The enthalpies and entropies for different M^{2+}-Kryptofix5 complexes in various AN-NM mixtures are listed in Table 1.

The change of the topology of the ligand from a linear conformation in the uncomplexed state to a helical conformation in the complex state leads to a large loss of entropy. This is supported by the experiment finding that the decrease of entropy due to complexation is smallest for the uptake of those cations, which do not induce steric deformation of the ligand structure [3].

The changes of the enthalpy of the ligand by complexation are mainly due to the changes of solvation, interamolecular ligand-ligand repulsion, the stacking of the aromatic residues and steric deformation of the ligand induced by the bound metal ion [12].

It is well known that the cryptands due to their high degree of flexibility and increased number of donating atoms in the macrocyclic ring can wrap themselves around the metal ions of proper size to form

Table 1: Formation constant, enthalpy and entropy for different Kryptofix5-M^{2+} complexes in various AN-NM mixtures at various temperatures.

Cation	wt% AN	Log K_f				ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	ΔG° (kJ mol^{-1})
		15 °C	25 °C	35 °C	45 °C			
Pb^{2+} (1.19 Å)	100[a]	6.81 ± 0.01	6.76 ± 0.02	6.71 ± 0.01	6.68 ± 0.02	-8 ± 1	103 ± 2	-38 ±1
	80	6.31 ± 0.03	6.30 ± 0.03	6.26 ± 0.03	6.14± 0.03	-9 ± 3	88 ± 10	-36 ± 4
	60	5.37 ± 0.07	5.55 ± 0.05	5.71 ± 0.03	5.78 ± 0.03	24 ± 3	188 ± 10	-32 ± 4
	40	4.67 ± 0.01	4.86 ± 0.09	4.97 ± 0.09	4.86 ± 0.09	12 ± 8	133 ± 28	-27 ± 12
Zn^{2+}(0.74 Å)	100[a]	6.81 ± 0.03	6.67 ± 0.02	6.59 ± 0.02	6.51 ± 0.02	-17 ± 2	70 ± 6	-38 ± 3
	80	6.49 ± 0.06	6.84 ± 0.06	6.40 ± 0.07	6.37 ± 0.07	-14 ± 18	80 ± 60	-37 ± 25
	60	6.72 ± 0.02	6.43± 0.03	6.60 ± 0.02	6.40 ± 0.02	-14 ± 10	79 ± 35	-37 ± 15
	40	6.71 ± 0.01	6.55 ± 0.02	6.38 ± 0.02	6.86 ± 0.03	4 ± 19	141 ± 64	-38 ± 27
Cu^{2+} (0.77 Å)	100[a]	6.59 ± 0.02	6.54 ± 0.02	6.51 ± 0.03	6.47 ± 0.03	-7 ± 0.5	103 ± 1	-37 ± 0.6
	80	6.37 ± 0.05	6.55 ± 0.03	6.43 ± 0.04	6.50 ± 0.06	5 ± 7	140 ± 22	-37 ± 9
	60	6.55 ± 0.03	6.44 ± 0.03	6.40 ± 0.04	6.56 ± 0.04	-0.5 ± 8	123 ± 25	-37 ± 11
	40	5.71 ± 0.02	5.87 ± 0.02	5.86 ± 0.04	5.87 ± 0.03	8 ± 5	139 ± 16	-33 ± 7
Co^{2+} (0.75 Å)	100[a]	5.85 ± 0.02	5.65 ± 0.03	5.45 ± 0.02	5.34 ± 0.03	-30 ±3	6 ± 9	-32 ± 4
	80	5.20 ± 0.05	5.23 ± 0.01	5.18 ± 0.01	5.29 ± 0.03	4 ± 4	112 ±12	-30 ± 5
	60	5.42 ± 0.02	4.99 ± 0.03	5.05 ± 0.03	5.04 ± 0.03	-19 ± 13	34 ± 44	-29 ± 19
	40	4.77 ± 0.04	4.98 ± 0.01	5.11 ± 0.02	5.18 ± 0.01	24 ± 4	175 ± 13	-28 ± 5
Ni^{2+} (0.69 Å)	100[a]	5.65 ± 0.01	5.54 ± 0.02	5.42 ± 0.01	5.31 ± 0.01	-20 ± 0.2	39 ± 1	-31 ± 0.4
	80	5.62 ± 0.01	5.25 ± 0.02	5.30 ± 0.02	5.26 ± 0.04	-18 ± 11	42 ± 36	-31 ± 15
	60	5.74 ± 0.02	5.23 ± 0.03	5.07 ± 0.04	4.95 ± 0.03	-45 ± 11	-47 ± 35	-31 ± 15
	40	5.00 ± 0.03	-	4.74 ± 0.03	4.73 ± 0.02	-17 ± 5	37 ± 17	-28 ± 7
Mn^{2+} (0.46 Å)	100[a]	6.40 ± 0.05	6.53 ± 0.04	6.10 ± 0.03	5.85 ± 0.07	-36 ± 14	0.1 ± 46	-36 ± 19
	80	5.49 ± 0.03	5.51 ± 0.03	5.58 ± 0.05	5.38 ± 0.06	-4 ± 7	91 ± 24	-31 ± 10
	60	5.32 ± 0.05	5.22 ± 0.03	5.32 ± 0.05	5.36 ± 0.05	4 ± 5	114 ± 17	-30 ± 7
	40	4.58 ± 0.09	4.84 ± 0.09	5.08 ± 0.04	5.23 ± 0.04	38 ± 3	222 ± 10	-28 ± 4

[a] *Reference [6]*

Table 2: Formation constant for different Kryptofix5-M2+ complexes in various AN-MeOH mixtures at 25 °C.

wt% AN	Log K_f				
	Pb^{2+}	Zn^{2+}	Cu^{2+}	Co^{2+}	Ni^{2+}
100[a]	6.76 ± 0.01	6.67 ± 0.02	6.54 ± 0.02	5.65 ± 0.04	5.54 ± 0.02
80	6.50 ± 0.02	5.89 ± 0.01	6.65 ± 0.01	6.15 ± 0.02	5.14 ±0.01
60	6.25 ± 0.02	4.35 ± 0.01	6.41 ± 0.01	4.59 ± 0.01	3.52 ±0.01
40	6.24 ± 0.01	4.37 ± 0.01	6.27 ± 0.01	4.53 ± 0.01	4.41 ± 0.01
0	4.21 ± 0.02	2.99 ± 0.01	4.28 ± 0.02	3.57 ± 0.01	3.24 ± 0.01

[a] *Reference [6]*

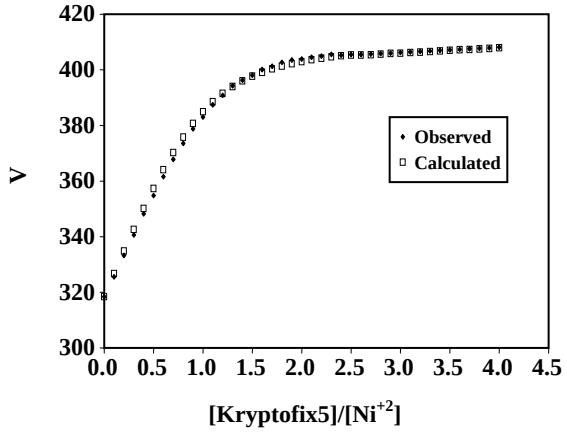

Fig. 5: Computer fit of the molar conductance-mole ratio data for the Kryptofix5-Ni^{2+} systesm at 25°C in 60% AN-40% NM.

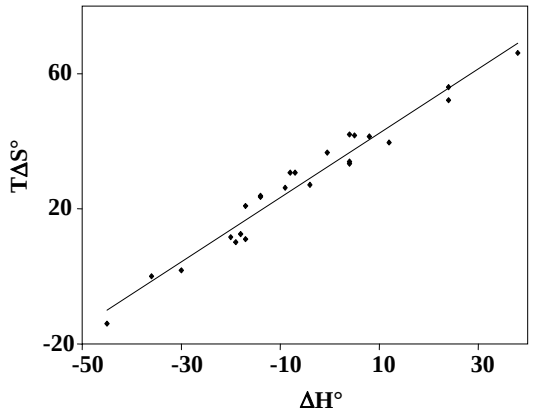

Fig. 6: Plot of TΔS° (kJ mol^{-1}) vs. ΔH° (kJ mol^{-1}) for 1:1 complexation of Zn^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Mn^{2+} and Cu^{2+} ions with Kryptofix5 in different AN–NM binary mixtures.

tridimensional wrap around complexes, in which all donating atoms of the ring are coordinated to the central cation. In this case, the size of cation is expected to influence strongly the extent of complex formation. The thermodynamic data given in Table 1 show that, in some cases, the complexes are enthalpy and entropy stabilized [13]. The data given in Table 1 clearly illustrate the fundamental role of the solvent properties in the M^{2+}-Kryptofix5 complexation reactions. In the case of all metal ions, the stability of the resulting complexes with Kryptofix5 decreases with increasing weight percent of NM and MeOH in the solvent mixture. Table 1 shows that, as expected, for all M^{2+}-Kryptofix5 systems, the thermodynamic data vary significantly with the solvent properties. However, in all cases, the observed increase (or decrease, depending on the nature of the metal ion) in ΔH° value upon addition of NM to the solvent mixture will be compensated by an increase (or decrease) in the corresponding ΔS° value. The existence of such a compensating effect (Fig. 6) between ΔH° and ΔS° values, which has been frequently reported for a variety of metal-ligand systems [14-16], would cause the overall change in the ΔG° value of the complex to be smaller than might be expected from the change in either ΔH° or ΔS° independently.

CONCLUSIONS

From the cunductomeric results obtained on the thermodynamics of complexation of Kryptofix5 with transition and heavy metal ions in different AN–NM and AN-MeOH binary mixtures it can be concluded that:

1. Kryptofix5 forms stable complexes with transition and heavy metal ions due to its high degree of flexibility and donating atoms in the macrocyclic ring.

2. The solvent illustrate the fundamental role of in the M^{2+}-Kryptofix5 complexation reactions. In the case of all metal ions, the stability of the resulting complexes with Kryptofix5 decreases with increasing weight percent of NM and MeOH in the solvent mixture.

3. Although the enthalpy and entropy changes are strongly solvent dependent, the observed increase (or decrease, depending on the nature of the metal ion) in ΔH° value upon addition of NM to AN will be compensated by an increase (or decrease) in the corresponding ΔS° value.

Received : Jan. 2, 2011 ; Accepted : Nov. 28, 2011

REFERENCES

[1] Moore C., Pressman B.C., Mechanism of Action of Valinomycin on Mitochondria, *Biochem. biophys. Res. Commun.*, **15**, p. 562 (1964).

[2] Tuemmler B., Maass G., Weber E., Wehner W., Voegtle, F., Noncyclic Crown-Type Polyethers, Pyridinophane Cryptands, and Their Alkali Metal Ion Complexes: Synthesis, Complex Stability, and Kinetics, *J. Am. Chem. Soc.*, **99**, p. 4683 (1977).

[3] Tummler B., Maass G., Vogtle F., Sieger H., Heimann U., Weber E., Open-Chain Polyethers. Influence of Aromatic Donor End Groups on Thermodynamics and Kinetics of Alkali Metal Ion Complex Formation, *J. Amer. Chem. Soc.*, **101**, p. 2588 (1979).

[4] Madrakian T., Shamsipur M., Spectrophotometric Study of Some Transition Metal Complexes with Tetraethyleneglycol-bis-(8-quinolyl) Ether in Dimethylsulfoxide Solution Using Murexide as a Metallochromic Indicator, *Polish J. Chem.*, **73**, p. 1405 (1999).

[5] Rofouei M.K., Ahmadalinezhad A., Taghdiri M., Complexation Thermodynamics of Some Alkali-Metal Cations with 1,13-Bis(8-Quinolyl)-1,4,7,10,13-Pentaoxatridecane in Acetonitrile, *J. Incl. Phenom.*, **58**, p. 377 (2007).

[6] Payehghadr M., Zamani A., Salehi Sadaghiani A., Taghdiri M., Spectrophotometric and Conductometric Studies of the Thermodynamics Complexation of Zn^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+} and Cu^{2+} Ions with 1,13-Bis(8-Quinolyl)-1,4,7,10,13-Pentaoxatridecane Ligand in Acetonitrile Solution., *J. Incl. Phenom.*, **62**, p. 255 (2008).

[7] Greenberg M.S., Popov A.I., Spectroscopic Studies of Ionic Solvation- XVII Studies of Preferential Solvation of the Sodium Ion in Nonaqueous Mixed Solvents by Sodium-23 Nuclear Magnetic Resonance, *Spectrochim. Acta Part A*, **31**, p. 697 (1975).

[8] Wu Y.C., Koch W.F., Absolute Determination of Electrolytic Conductivity for Primary sStandard KCl Solutions from 0 to 50°C, *J. Solution Chem.*, **20**, p. 391 (1991).

[9] Amini M.K., Shamsipur M., Complex Formation of Silver, Thallium and Alkali Cations with Dibenzo-30-Crown-10 in Some Non-Aqueous Solutions, *Inorg. Chim. Acta*., **183**, p. 65 (1991).

[10] Amini M.K., Shamsipur M., Complex Formation of Hydronium Ion with Several Crown Ethers in 1,2-Dichloroethane, Acetonitrile, and Nitrobenzene Solutions, *J. Solution Chem.*, **21**, p. 275 (1992).

[11] Ganjali M.R., Rouhollahi A., Moghimi, A., Shamsipur, M., Conductance Study of Alkali Metal Complexes with 4¢-Carboxy-Benzo-24-Crown-8 and 4¢-Amido-Benzo-24-Crown-8 in Nitromethane, Acetonitrile and Dimethyle Formamide Solutions, *Pol. J. Chem.***, 70**, p. 1172 (1996).

[12] Weber E., Toner J.L., Goldberg I., Voegtle F., Laidler D.A., Stoddart J.F., Bartsch R.A., Liotta, C.L., "Crown Ethers and Analogs". Wiley (1989).

[13] Pourghobadi Z., Seyyed-Majidi F., Daghighi-Asli M., Parsa F., Moghimi A., Ganjali M.R., Aghabozorgand H., Shamsipur M., Synthesis of a New Triazine Derived Macrocycle and a Thermodynamic Study of Its Complexes with Some Transition and Heavy Metal Ions in Acetonitrile Solution, *Pol. J. Chem.*, **74**, p. 837 (2000).

[14] Takeda Y., Thermodynamic Study for Dibenzo-24-Crown-8 Complexes with Alkali Metal Ions in Nonaqueous Solvents, *Bull. Chem. Soc. Jpn.,* **56**, p. 3600 (1983).

[15] Gutmann V., "The Donor-Acceptor Approach to Molecular Interactions", Plenum, New York, (1978).

[16] Taghdiri M., Rofouei M.K., Shamsipur M., Conductance Study of the Thermodynamics of Complexation of K^+, Rb^+, Cs^+ and Tl^+ Ions with Dibenzo-24-Crown-8 in Binary Acetonitrile-Nitromethane Mixtures, *J. Incl. Phenom.*, **58**, p. 181 (2007).