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Research Article

Conductometric Studies of Thermodynamics of Complexation of Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} Cations with Aza-18-crown-6 in Binary Acetonitrile-Methanol Mixtures

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The complexation reactions between aza-18-crown-6 (A18C6) and Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions were studied conductometrically in different acetonitrile-methanol mixtures at various temperatures. The formation constants of the resulting 1 : 1 complexes were calculated from the computer fitting of the molar conductance-mole ratio data at different temperatures. Selectivity of A18C6 for Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} cations is sensitive to the solvent composition. At 20°C and in acetonitrile solvent, the stability of the resulting complexes varied in the order $Zn^{2+} > Cu^{2+} > Co^{2+} \sim Ni^{2+}$ but the order was reversed by adding 20% methanol. The enthalpy and entropy changes of the complexation reactions were evaluated from the temperature dependence of formation constants. It was found that the stability of the resulting complexes decreased with increasing methanol in the solvent mixture. The $T\Delta S^\circ$ versus ΔH° plot of thermodynamic data obtained shows a fairly good linear correlation indicating the existence of enthalpy-entropy compensation in the complexation reactions. In addition, binding energies of Ni^{2+}, Cu^{2+}, and Zn^{2+} complexes with A18C6 were calculated at B3LYP/6-31G level of theory.

1. Introduction

Macrocyclic polyethers (crown ethers), first prepared in the 1960s [1], constitute an important class of host molecules that have found broad application to studies of molecular recognition and inclusion phenomena [2]. They are macrocycles capable of ion encapsulation due to their cage like structures. The metal ion is held in the crown ether cavity by electrostatic attraction between the charged cation and dipoles created by the nonbonding electrons of donor atoms [3, 4]. The selectivity and stability of crown ethers are also influenced by their structural flexibility, the number and type of donor atoms on the cavity of the crown, and the solvation energy of the metal ion. Thus, compounds of this type have been used extensively for selective complexation and transport of cations, anions, and neutral molecules [5]. Macrocyclic crown compounds have gained a great deal of attention due to their wide applications in chemistry [6] such as microanalysis, sensing and separation of metal ions [7], and extraction of biogenic amines [8].

Aza-crown ethers have especially been focused on as useful ligands because of their versatility and applicability [8–11]. It was of interest to us to study the interaction of the various cations with aza-crown ethers. Since the nature of these compounds, the size of cavity, and solvent may strongly influence the stoichiometry and complexation of transition metal complexes in solution [6], the complexation reactions between aza-18-crown-6 (A18C6) (Figure 1) with Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions were studied by conductometric in acetonitrile (AN) and different acetonitrile-methanol (MeOH) mixtures at various temperatures. The formation constants of the resulting 1 : 1 complexes were calculated from the computer fitting of the molar conductance-mole ratio data at different temperatures. Little work has been reported on the study of the stability of transition and heavy metal ion complexes with A18C6, mainly in binary

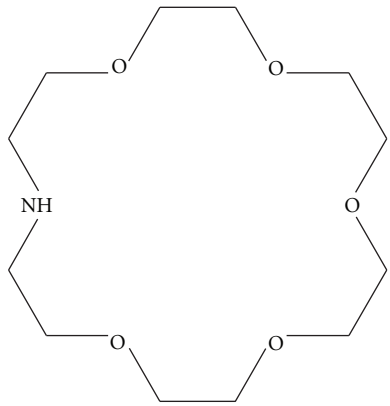

Figure 1: Structure of aza-18-crown-6.

solvent mixtures [12–14]. Thus, studies of complexation reactions as a function of the solvent composition in binary solvent mixtures might be used to investigate the factors contributing to the changes in complexation stability and selectivity of the resulting complexes [11–13]. It should be noted that AN and MeOH have different Gutmann donor numbers, (DN) (i.e., for AN, DN = 14.1, and for MeOH, DN = 19.0) [15]. The Gutmann donor numbers are a measure of the electron-donating properties of a solvent. The donor number is defined as the negative enthalpy value for the 1 : 1 adduct formation between a given electron-pair donor solvent and the standard Lewis acid $SbCl_5$, in dilute solution in the non-coordinating solvent 1,2-dichloroethane, for which a DN of zero is assigned. DN reflects the ability of the solvent to solvate cations and other Lewis acids. DN values range from zero, for solvents like hexane or tetrachloromethane, to 61.0 for triethylamine. In general, it is observed that the smaller the values of DN, the more stable the cation-crown ether complex [6].

2. Experimental

Reagent-grade nitrate salts of cobalt, nickel, copper, and zinc, dried acetonitrile ($H_2O < 0.005\%$) and methanol (all from Merck) were of the highest purity available and used as received. A18C6 was purchased from Fluka. All the AN-MeOH mixtures used were prepared by weight.

Conductance measurements were carried out with a Metrohm 712 conductivity meter. A dip-type conductivity cell made of platinum black was used. The cell constant at the different temperatures used was determined by conductivity measurements of a 0.010 M solution of analytical-grade KCl (Merck) in triply distilled deionized water. The specific conductance of this solution at various temperatures has been reported in the literature [16]. In all measurements, the cell was thermostated at the desired temperature $\pm 0.1^\circ$C using a Haake D1 thermostat-circulator water bath.

In a typical experiment, 10 mL of the desired metal ion (5.0×10^{-5} M) was placed in the titration cell, thermostated to the desired temperature and the conductance of solution was measured. Then, a known amount of a concentrated A18C6 solution (5.0×10^{-3} M) was added in a stepwise manner using a calibrated micropipette. The conductance of the solution was measured after each addition. The ligand solution was continually added until the desired ligand to cation mole ratio was achieved. The dilution of the salt solution during the titration is negligible because the total volume of added concentrated A18C6 solution is 300 μL. Therefore, the conductance changes during the titration due to the dilution are very negligible and are neglected.

NMR spectra in deuterated acetonitrile (CD_3CN) were recorded on a Bruker Avance 300 spectrometer, and all chemical shifts are reported in δ units downfield from Me_4Si. In a typical measurement, 0.5 mL of ligand solution (0.02 M) in CD_3CN was placed in the 5 mm BBO NMR tube and the spectrum was recorded. Then a known amount of a concentrated solution of zinc nitrate (0.2 M) in CD_3CN was added in a stepwise manner using a 10-μL Hamilton syringe and the spectrum of the solution was recorded after each addition. The zinc ion solution was continually added until the desired cation to ligand molar ratio was achieved.

The formation constants, K_f, and the limiting molar conductances, Λ_o, of the resulting 1 : 1 complexes between A18C6 and the cations used, in different AN-MeOH mixtures and at various temperatures, were calculated by fitting the observed molar conductance, Λ_{obs}, at varying [A18C6]/[M^{2+}] mole ratios to a previously derived equation [6, 17, 18] which expresses the Λ_{obs} as a function of the free and complexed metal ions. A nonlinear least squares curve fitting using Microsoft Excel Solver (version 11.0) was applied for the evaluation of formation constant and limiting molar conductance of the resulting 1 : 1 complexes. The large formation constant values ($\log K_{ML} > 6$) can be determined by this method.

Chi-square statistic was used to evaluate the fitness of equation to the experimental data. The Chi-square test statistic is the sum of the squares of the differences between the experimental data and data obtained by calculating from equation. The equivalent mathematical statement is

$$\chi^2 = \sum_{i=1}^{N} \frac{\left(\Lambda_{\text{exp.}} - \Lambda_{\text{calc.}}\right)^2}{\Lambda_{\text{calc.}}}, \tag{1}$$

where $\Lambda_{\text{exp.}}$ and $\Lambda_{\text{calc.}}$ are the molar conductance obtained by experimental data and calculating from the equation, respectively. If calculated data are similar to the experimental data, χ^2 will be a small number; if they are different, χ^2 will be a large number.

3. Results and Discussion

The conductometric method has been extensively used for obtaining the formation constants of complexes of crown ethers with metal cations [6]. In order to evaluate the influence of adding A18C6 on the molar conductance of Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions in different AN-MeOH mixtures, the molar conductance at a constant salt concentration (5.0×10^{-5} M) was monitored while increasing the crown ether concentration at various temperatures. Some of the resulting molar conductances versus A18C6/cation mole ratio plots are shown in Figures 2 and 3.

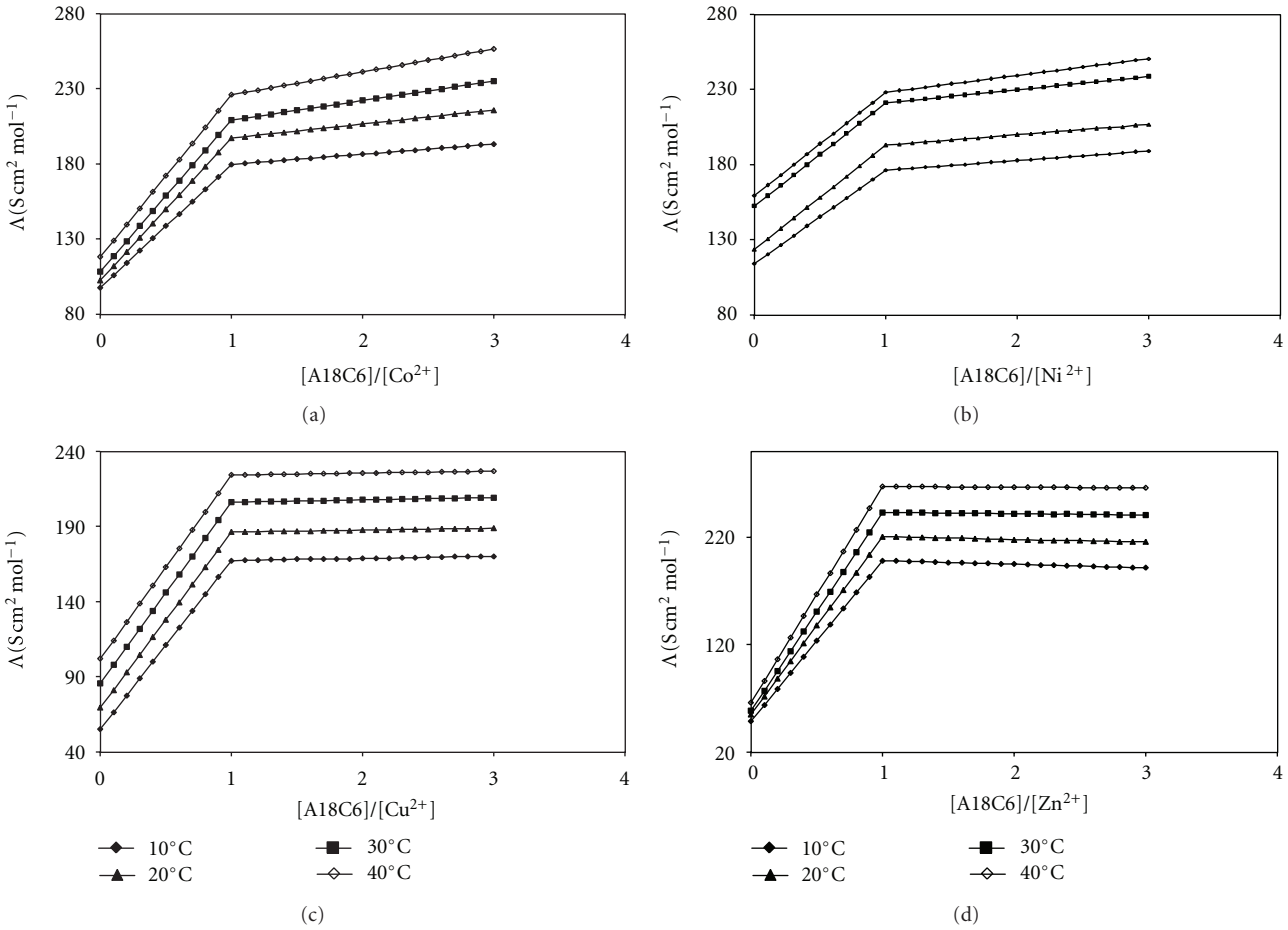

Figure 2: Molar conductance (S cm^2 mol^{-1}) versus [A18C6]/[M^{2+}] mole ratio plots in 100% AN at various temperatures. The M^{2+} cations are (a) Co^{2+}, (b) Ni^{2+}, (c) Cu^{2+} and (d) Zn^{2+}.

As it is seen, in all cases, there is a gradual increase in the molar conductance with an increase in the crown ether concentration. Figure 2 shows that, in the case of all M^{2+}-A18C6 system in AN solvent, the addition of A18C6 to the M^{2+} ion solution causes a continuous increase in the molar conductance, which begins to level off at a mole ratio greater than one. Such a conductance behavior is indicative of the formation of fairly stable 1 : 1 complexes in AN.

The formation constants of all A18C6-M^{2+} complexes in different solvent mixtures at various temperatures, obtained by computer fitting of the molar conductance-mole ratio data and Chi-square values (χ^2), are listed in Table 1. The computer fits of the molar ratio data are shown as solid lines. The small numbers of Chi-square indicate that our assumption of 1 : 1 stoichiometry seems reasonable in the light of the fair agreement between the observed and calculated molar conductances.

In order to have a better understanding of the thermodynamics of complexation reactions of Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions with A18C6, it is useful to investigate the enthalpic and entropic contributions to these reactions. The ΔH° and ΔS° of the complexation reactions in different AN-MeOH mixtures were evaluated from the temperature dependence of the formation constants by applying a linear least-squares analysis according to the van't Hoff equation. The van't Hoff plots of log K_f versus $1/T$ are shown in Figure 4. The enthalpies and entropies of complexation were determined in the usual manner from the slopes and intercepts of the plots, respectively and the results are listed in Table 2.

In the case of complexation of macrocyclic ligands, there are many factors which can make significant contributions to the stability of their metal ion complexes: the cation size, the ionic solvation of the charged species involved, conformations of the free and complexed crown ethers, the electronic structure of metal ion and the binding strengths of solvent-ion and crown-ion. Moreover, the changes of the enthalpy and entropy influence the stability constant. Many factors contribute to changes in enthalpy and entropy of complexation reactions. It seems that solvent properties such as donor number, relative permittivity (dielectric constant) and their dipole moments influence upon the enthalpy and entropy.

The data given in Table 1 clearly illustrate the fundamental role of the solvent properties in the M^{2+}-A18C6 complexation reactions studied. The stability of the resulting complexes decreases strongly with increasing weight percent

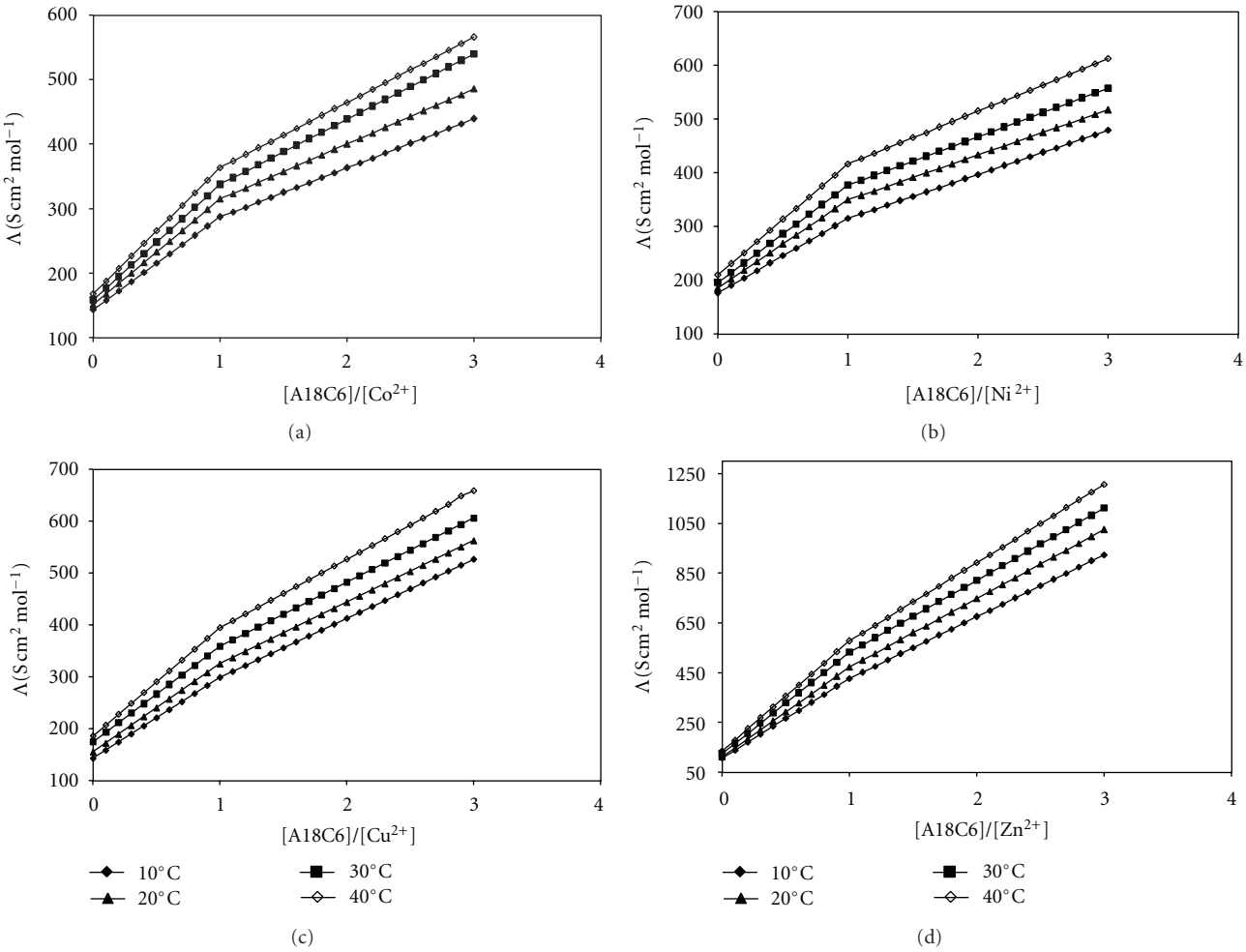

Figure 3: Molar conductance (S cm^2 mol^{-1}) versus [A18C6]/[M^{2+}] mole ratio plots in AN-MeOH (80 : 20) mixture at various temperatures. The M^{2+} cations are (a) Co^{2+}, (b) Ni^{2+}, (c) Cu^{2+}, and (d) Zn^{2+}.

Table 1: Formation constants for different M^{2+}-A18C6 complexes in various AN-MeOH mixtures.

Cation[a]	wt% AN	Log K_f							
		10°C	χ^2	20°C	χ^2	30°C	χ^2	40°C	χ^2
Co^{2+} (1.50)	100	5.66	0.76	5.50	1.11	5.27	1.48	5.19	1.69
	80	3.87	1.60	3.89	1.95	3.79	1.87	3.90	2.41
	60	2.82	0.10	2.90	0.15	2.98	0.25	2.91	1.35
	40	2.83	0.11	2.87	0.14	2.83	0.15	2.86	0.25
Ni^{2+} (1.38)	100	5.47	0.54	5.49	0.60	5.28	0.63	5.05	0.72
	80	3.73	1.09	3.91	1.81	3.95	2.14	4.00	2.72
	60	2.90	0.12	2.94	0.18	3.06	0.69	3.14	0.44
	40	2.96	0.17	2.99	0.21	3.01	0.23	3.06	0.30
Cu^{2+} (1.54)	100	7.44	0.09	7.77	0.07	7.48	0.09	7.63	0.07
	80	3.39	0.71	3.47	0.94	3.53	1.16	3.63	1.73
	60	3.11	0.31	3.14	0.37	3.17	0.45	3.20	0.77
	40	3.08	0.30	3.06	0.29	3.03	0.27	3.02	0.28
Zn^{2+} (1.48)	100	15.27	0.64	14.60	0.29	14.33	0.07	14.07	0.01
	80	3.25	1.43	3.31	1.72	3.44	2.99	3.46	3.17
	60	2.96	0.75	3.04	0.79	3.13	1.31	3.18	1.66
	40	1.44	1.82	1.93	0.008	2.44	0.12	2.82	0.75

[a]The values in parenthesis are the ionic sizes in Å [19].

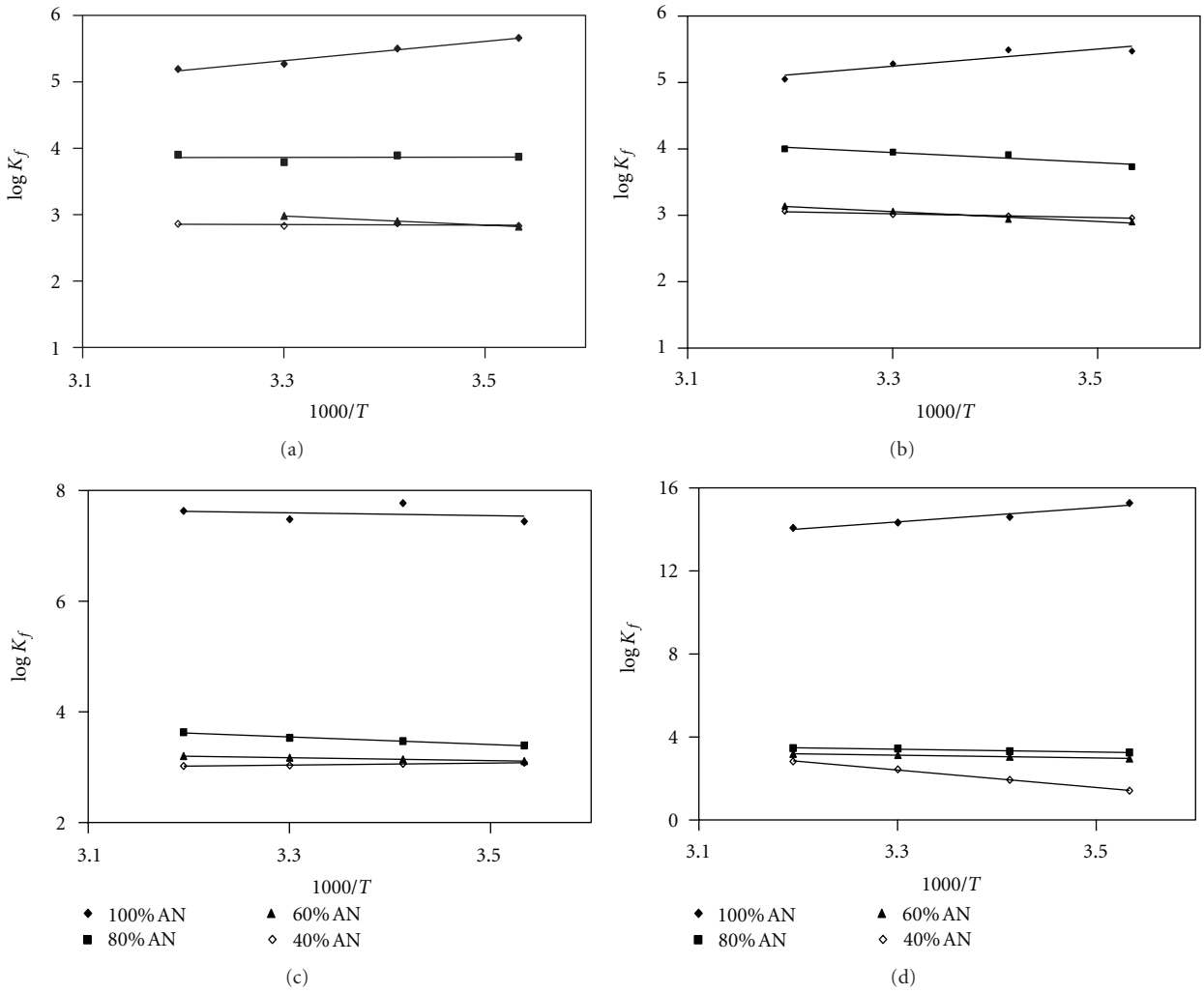

Figure 4: van't Hoff plots for the 1 : 1 complexation of Co^{2+} (a), Ni^{2+} (b), Cu^{2+} (c), and Zn^{2+} (d) with A18C6 in different solvent mixtures.

of MeOH in the solvent mixture (Figure 5). It is well known that the solvating ability of the solvent, as expressed by the Gutmann donor number [15], plays an important role in different complexation reactions [4, 16, 18, 20, 21]. There is actually an inverse relationship between the stabilities of the complexes and the solvating abilities of the solvents. Methanol has a higher donicity (DN = 19.0) than acetonitrile (DN = 14.1) and, therefore, shows more competition with the crown ether for mentioned ions; thus, it is not unexpected to observe that addition of methanol to acetonitrile will decrease the stability of the complexes. In addition, selectivity for certain cations over others may be altered according to the nature of solvent. The order of stability of complexes in pure AN at 20°C is $Zn^{2+} > Cu^{2+} > Co^{2+} \sim Ni^{2+}$. It is interesting to note that the order of the stability of the complexes formed between A18C6 and these metal cations in AN-MeOH (wt% MeOH = 20) binary mixtures is reversed. This reversal of stabilities indicates the selectivity of macrocyclic ligands is sensitive to the solvent composition and may change in certain composition of the mixed solvent systems. A reversal in stabilities has been observed for M^{n+}-A18C6 (M^{n+} = Ag^{+}, Hg^{2+} and Pb^{2+}) in DMSO-H_2O binary mixture [13]. The selectivity of complexation not only depends on the ratio of the cation diameter and the diameter of the crown ether cavity, but also on the solvent composition. The change of solvent composition influences upon the changes in complexation enthalpies and entropies and hence the selectivity of the crown ethers towards cations. It seems that solvent properties such as donor number, dielectric constant and the isosolvation point (the point at which both solvents participate equally in the inner salvation shell of the cation [22]) contribute to the changes of enthalpy and entropy as a function of solvent composition.

Table 2 shows that, as expected, for M^{2+}-A18C6 systems studied, the thermodynamic data vary significantly with the solvent properties. However, the observed increase (or decrease, depending on the nature of the metal ion) in ΔH° value upon addition of MeOH to the solvent mixture will be compensated by an increase (or decrease) in the corresponding ΔS° value. The existence of such a compensating effect (Figure 6) between ΔH° and ΔS° values, which has been frequently reported for a variety of metal-ligand systems

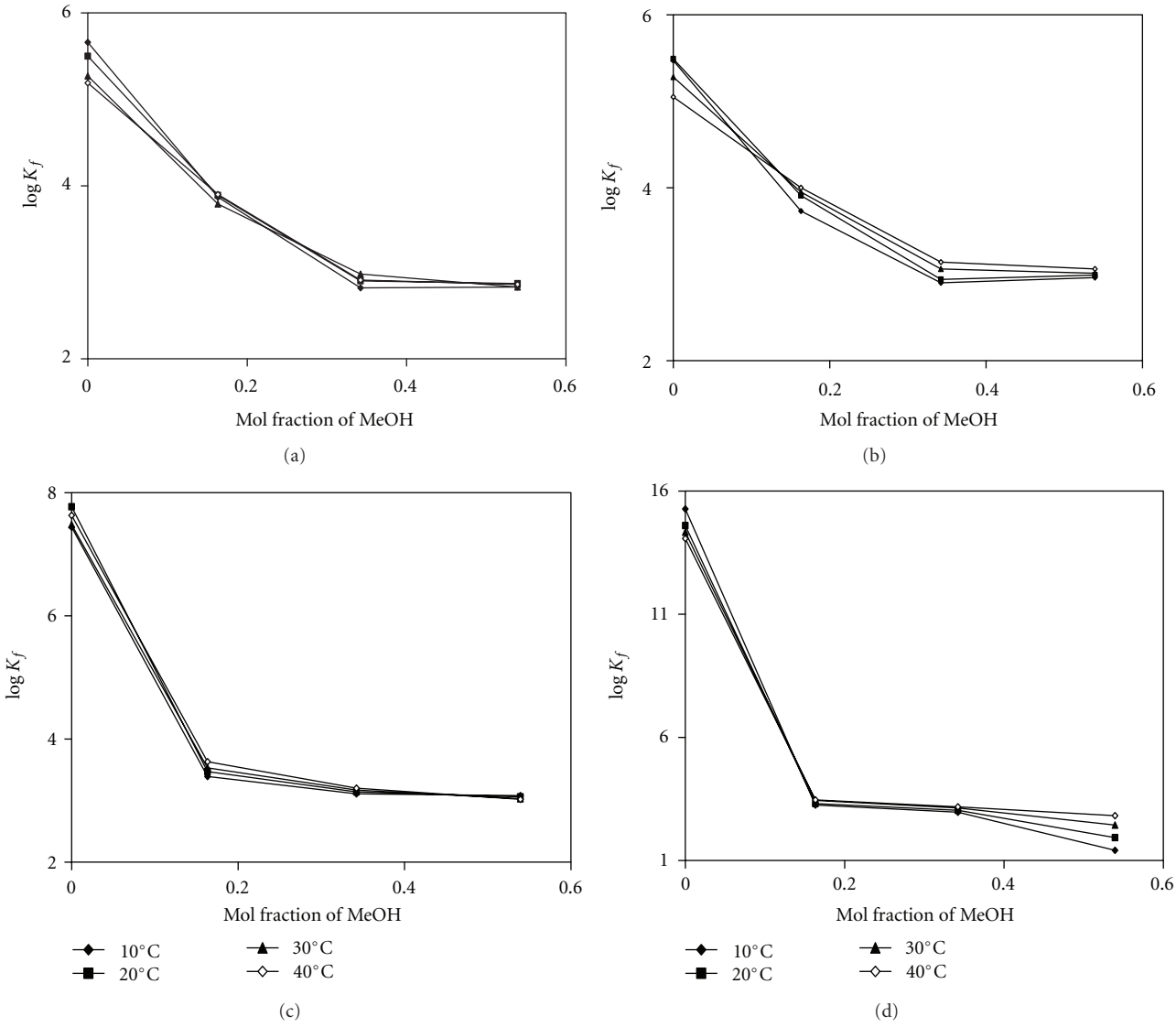

Figure 5: Variation of the stability constants of various A18C6-M^{2+} systems with the composition of the AN-MeOH binary mixture at different temperatures. The M^{2+} cations are (a) Co^{2+}, (b) Ni^{2+}, (c) Cu^{2+}, and (d) Zn^{2+}.

[23–25], 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. There is an entropy-driven stabilization for Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} complexation in AN-MeOH mixtures. These cations have small ionic sizes (Table 1) and are strongly solvated by MeOH. Therefore, complete or partial desolvation of cations and ligand are important steps of complexation process and seems to be mainly responsible for increasing of entropy.

The stability constant between Zn^{2+} and A18C6 is much greater in AN than other studied cations. It also shows a slight decrease in the molar conductance after the mole ratio of one (Figure 2(d)). Therefore, the ^{1}H NMR spectra of a 0.02 M solution of A18C6 in deuterated AN in the presence of increasing concentration of zinc nitrate were recorded (Figure 7(a)). The resulting chemical shift versus metal ion to ligand mole ratio (shown in Figure 7(b)) revealed a distinct inflection point at a mole ratio of 1 : 2, indicating the formation of a ML_2 complex in solution. A sandwich type complex has been proposed for biphenyl containing A18C6 with Zn^{2+} from ^{1}HNMR, UV visible and fluorescence observations in AN [9]. The ML_2 complexes have been also proposed for 18C6-Cu^{2+} in methanol [26], A18C6-Pb^{2+} in H_2O, A18C6-Ag^+ in DMSO-H_2O [13], and immobilized DB18C6-Zn^{2+} [27].

An attempt was made to obtain more information from the quantum chemical calculations about the structures of both free and complex forms of A18C6. To do this, the initial structures of compounds were built with HyperChem 7.0 program [28]. All calculations were done with Gaussian 2003 suit of programs [29] on an Intel SMP computer with 8 processors and 8 GB of RAM. B3LYP/6-31G level of theory was used for all optimization and frequency calculations. All computations were done in the gas phase. Full geometry

Table 2: Thermodynamic parameters for different M^{2+}-A18C6 complexes in various AN-MeOH mixtures.

Cation	wt% AN	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	ΔG° (kJ mol^{-1})
Co^{2+}	100	-27.9 ± 3.3	9.8 ± 11.1	-30.8 ± 4.7
	80[a]	1.6 ± 0.6	79.8 ± 2.0	-21.8 ± 0.8
	60[b]	13.1 ± 0.3	100.4 ± 1.1	-16.3 ± 0.5
	40[c]	1.6 ± 0.8	59.6 ± 2.7	-15.9 ± 1.1
Ni^{2+}	100	-24.6 ± 7.5	19.2 ± 25.3	-30.2 ± 10.7
	80	14.6 ± 3.7	123.5 ± 12.4	-21.6 ± 5.2
	60	14.2 ± 2.0	105.3 ± 6.7	-16.7 ± 2.8
	40	5.4 ± 0.8	75.7 ± 2.5	-16.8 ± 1.1
Cu^{2+}	100	—[d]	—[d]	—[d]
	80	13.2 ± 1.0	111.5 ± 3.2	-19.5 ± 1.4
	60	5.1 ± 0.1	77.5 ± 0.3	-17.6 ± 0.1
	40	-3.6 ± 0.4	46.3 ± 1.5	-17.2 ± 0.6
Zn^{2+}	100[e]	-46.5 ± 0.5	120.8 ± 1.6	-81.9 ± 0.7
	80	12.9 ± 2.4	107.9 ± 8.1	-18.7 ± 3.4
	60	12.7 ± 0.9	101.7 ± 3.1	-17.1 ± 1.3
	40	80.5 ± 3.3	311.7 ± 11.0	-10.8 ± 4.6

[a]Without considering Log K_f at 30°C.
[b]Without considering Log K_f at 40°C.
[c]Without considering Log K_f at 20°C.
[d]High uncertainty.
[e]Without considering Log K_f at 10°C.

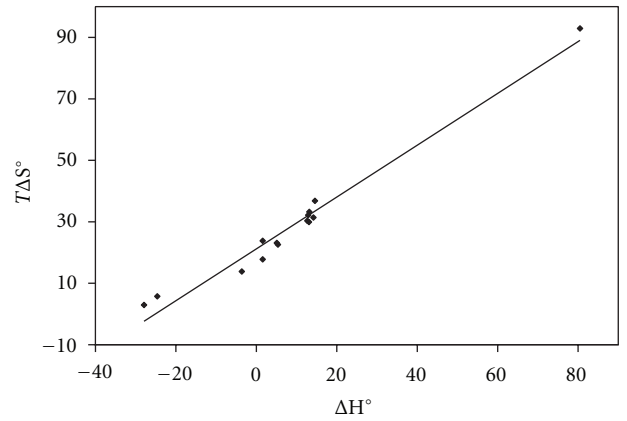

Figure 6: Plot of $T\Delta S^\circ$ (kJ mol^{-1}) versus ΔH° (kJ mol^{-1}) for 1 : 1 complexation of Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions with A18C6 in different AN-MeOH binary mixtures ($R = 0.987$).

Table 3: Calculated electronic energies of different species and binding energies of complexes formed by interaction between A18C6 and Ni^{2+}, Cu^{2+}, and Zn^{2+}. All calculations have been done with B3LYP/6-31G.

Compounds	Electronic energy (a.u.)	Binding energy (kcal/mol)[a]
A18C6	−903.07162832	
Ni^{2+}	−1507.14512292	
Cu^{2+}	−1639.396656	
Zn^{2+}	−1778.31513190	
A18C6-Ni^{2+}	−2410.87730681	−414.50
A18C6-Cu^{2+}	−2543.10355707	−398.64
$(A18C6)_2$-Zn^{2+}	−3585.13086395	−422.56

[a]Binding energy (ΔE) is defined as ΔE = E(complex)−E(Ligand)−E(Ion). 1 a.u. is equal to 627.5095 kcal/mol.

optimization was used with no symmetry or any constraints about bond lengths, bond angles, or bond torsions. Figure 8 shows the optimized geometries of both free and metal ion complexes of A18C6. Frequency analyses were done to test whether the optimized structures are stationary points or saddle points. In all outputs, number of imaginary frequency was equal to zero. This indicates that all structures are true optimized forms. Table 3 shows binding energies for A18C6-cation complexation for three metal cations of Ni^{2+}, Cu^{2+}, and Zn^{2+}. Despite many attempts, we could not obtain binding energies for A18C6-Co^{2+}. All binding energies are less than zero. It shows that all cations tend to form complex with A18C6 in the gas phase. It should be noted that these cations have relatively close ionic radii. The ML_2 structure for A18C6-Zn^{2+} (Figure 8(d)) indicates the strong interaction of Zn^{2+} with nitrogen atoms. The ^{1}HNMR study (Figure 7(a)) confirms this strong interaction. The ^{1}HNMR signal at $\delta = 2.17$ ppm corresponding to N–H, disappears upon addition of Zn^{2+} to A18C6.

4. Conclusions

From the conductometric results obtained on the thermodynamics of complexation of A18C6 with some transition metal ions in different AN-MeOH binary mixtures and

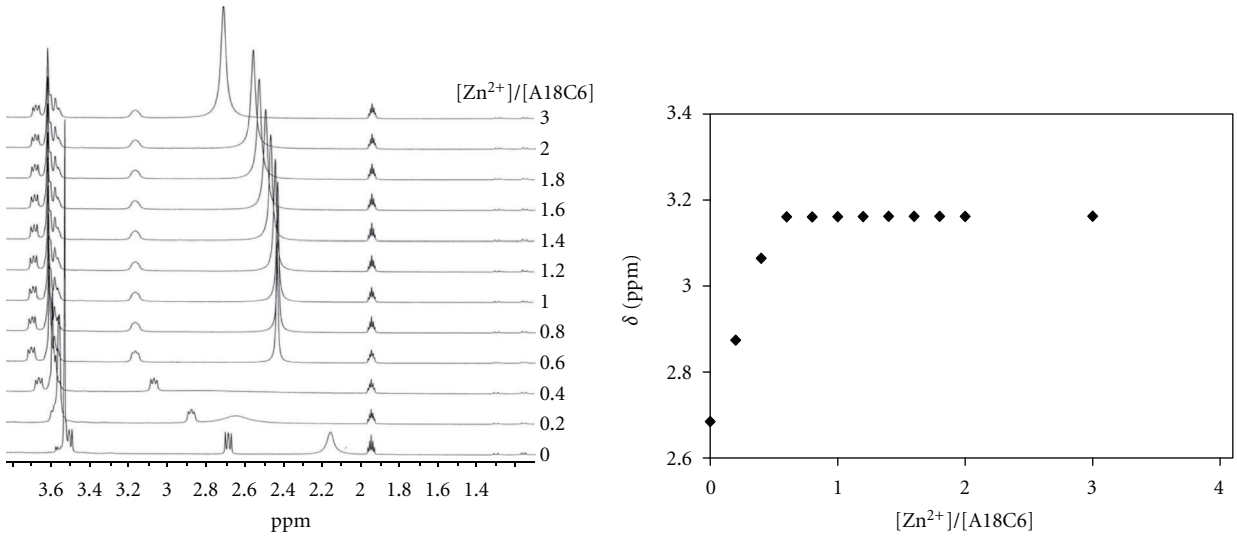

Figure 7: (a) The ^{1}HNMR spectra of A18C6 ligand in the presence of increasing concentration of Zn^{2+} ions in deuterated AN and (b) chemical shift versus $[Zn^{2+}]/[A18C6]$ plot.

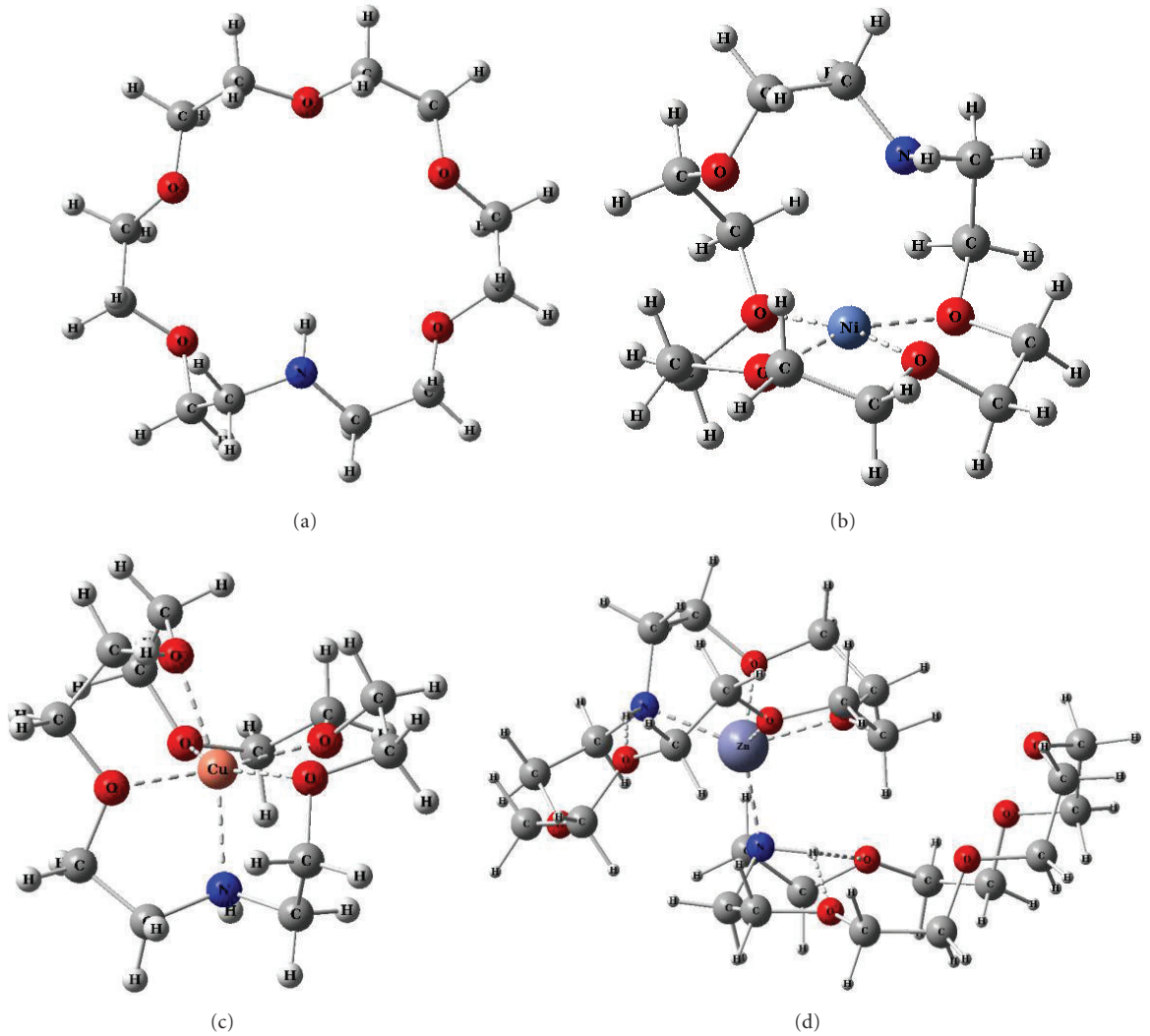

Figure 8: The optimized geometries of free A18C6 (a) and its complexes with Ni^{2+} (b), Cu^{2+} (c), and Zn^{2+}(d).

quantum chemical calculations, the following can be concluded.

(1) The solvent illustrate the fundamental role in the M^{2+}-A18C6 complexation reactions. In the case of all metal ions, the stability of the resulting complexes with A18C6 decreases and the order of stability vary with increasing MeOH in the solvent mixture.

(2) 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 MeOH to AN will be compensated by an increase (or decrease) in the corresponding ΔS° value.

(3) The quantum chemical calculations confirm the formation of stable A18C6-M^{2+} (M^{2+} = Ni^{2+} and Cu^{2+}) and $(A18C6)_2$- Zn^{2+} complexes.

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