



Conductance and Thermodynamic Study of the Interaction of Some Transition and Heavy Metals with Phenyl-aza-15-crown-5 (PhA15C5) in Different Binary Acetonitrile-Water Solvent Mixtures

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Abstract. A conductance study of the interaction between $\text{Fe}(\text{ClO}_4)_3$, $\text{Cu}(\text{ClO}_4)_2$, $\text{Fe}(\text{NO}_3)_3$, $\text{Cu}(\text{NO}_3)_2$, $\text{Hg}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2$ with phenyl-aza-15-crown-5 (PhA15C5) in different acetonitrile-water mixtures has been carried out at various temperatures. The formation constants were determined at various temperatures. It was found that the stability of the nitrate salts decreases in the order $\text{Hg}^{2+} > \text{Cu}^{2+} > \text{Fe}^{3+} > \text{Cd}^{2+}$ and the formation constants decrease as the percentage of acetonitrile decreases in the mixture. The counter anion also affects the stability of the complexes, where the metal perchlorate-crown complexes are more stable than those of the metal nitrate salts. The enthalpy and entropy of the complexation were calculated and were found to be sensitive to solvent composition.

Key words: phenyl-aza-15-crown-5, transition and heavy metals, mixed solvent, conductance, complex stability, enthalpy and entropy

1. Introduction

Interest in electrically-neutral complexing agents such as macrocyclic polyethers (crown-ethers) has increased continually since the original work of Pedersen [1–3]. Their affinity towards metal cations [4, 5], neutral molecules [6] and even anions [7] has led to intensive efforts to understand the factors that affect the thermodynamic and kinetic stability of the resulting complexes [8, 9]. The stability of crown complexes depends on several factors including the relative size of the cation and the macrocyclic cavity, the number and nature of binding sites, the acid-base character of metal ions, the counter anion and the nature of the solvent.

The use of crown-ethers was mainly concentrated on alkali, alkaline earth metals and on lanthanides. However, little work has been done on the complexation of transition and heavy metals with crown ethers [10–14]. Stability constants in

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methanol at 25 °C were calculated for the complexes of divalent cations Ni^{2+} , Zn^{2+} , Pb^{2+} , Co^{2+} and Cu^{2+} with 15C5, 18C6, dicyclohexano18C6 and dibenzo 24C8 [11]. It has been found that the stability constants were very low ($\log K_f$ 2.02–3.62).

In this sense, cations and crowns do not behave according to electrostatic attraction only. The transition metal ions and heavy metals favour the complexation with aza-crowns and thia-crowns much more than with the crown ethers. This is probably due to the polarized nature of these cations and their low affinity towards oxygen ligands [15].

In this respect, it was of interest to us to study the thermodynamics of the complexation of Fe^{3+} , Cu^{2+} , Hg^{2+} and Cd^{2+} with phenyl-aza-15-crown-5 (PhA15C5) and to study the effect of variables such as relative cation and ligand cavity size, nature of the cation, anion and the solvent properties on the selectivity and stability of these complexes.

2. Experimental

Phenyl-aza-15-crown-5 of highest purity was used as received. Reagent grade nitrate and perchlorate salts of iron, copper and the nitrate salts of mercury and palladium (Fluka) were of the highest purity available and used without any further purification, except for vacuum drying over P_2O_5 . Acetonitrile (from Gainland Chemical Company) was HPLC grade with 99.6% purity.

Triply distilled water was used with a specific conductivity less than 5×10^{-7} S cm^{-1} . Conductance measurements were carried out with a Metrohm E 518 conductivity meter. The cell constant at the different temperatures used were determined by measuring the conductivity of a solution of analytical grade KCl (BDH) in triply distilled water. In all measurements, the cell was thermostatted at the desired temperature ± 0.04 °C using a Haak Mess-Technik gmbh. U. Co. type F3, thermostat. In a typical experiment, 25 mL of the desired metal salt solution ($0.7 \times 10^{-4} - 2.0 \times 10^{-4}$ mol dm^{-3}) was placed in the titration cell thermostatted to the required temperature and the conductance of the solution was measured. Then, a known amount of another solution containing the same concentration of the metal salt and crown ether was added in a stepwise manner using a micropipette. After stirring and thermostating the solution, the conductance was measured after each addition. The same procedure was repeated until the desired ratio of cation to crown was attained.

The formation constants and the limiting molar conductances of the resulting complexes based on a 1 : 1 ratio in different AN- H_2O solvent mixtures at various temperatures were evaluated by fitting the observed molar conductance at various crown-to-metal ion mole ratios to an equation expressing the observed molar conductance as a function of the free and complexed metal ion. The formation constants were calculated by using a nonlinear least-squares program "Simplex"

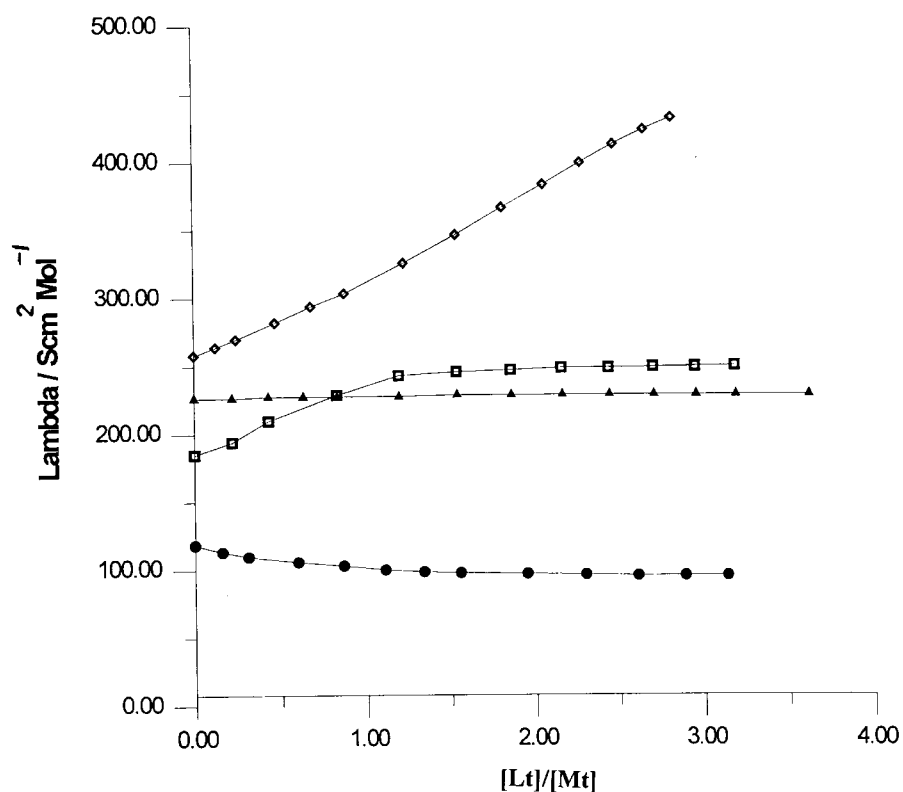


Figure 1. Molar conductance vs. $[L_T]/[M_T]$ curves for metal nitrate-crown complexes in 95% AN-H₂O at 25 °C. ◇, Fe(NO₃)₃; □, Cu(NO₃)₂; ▲, Cd(NO₃)₂; ●, Hg(NO₃)₂ in 80% AN-H₂O.

reported elsewhere [16]. Least squares of $\log K$ vs. $1/T$ data was carried out using a linear fitting programme.

3. Results and Discussion

The molar conductance of the nitrate salts of Cu²⁺, Fe³⁺, Hg²⁺ and Cd²⁺ and the perchlorate salts of Cu²⁺ and Fe³⁺ in different AN-H₂O solvent mixtures was monitored as a function of PhA15C5 to metal ion mole ratio at various temperatures. The resulting molar conductance-mole ratio plots at 25 °C and in 95% AN-H₂O solvent mixture are shown in Figures 1 and 2.

It is obvious from Figure 1 that the addition of crown ether to Cu²⁺ and Fe³⁺ nitrate solution causes a continuous increase in the molar conductance which begins to level off at a mole ratio about unity. The slope of the corresponding mole ratio plots changes at the point where the crown-to-cation mole ratio is equal to one, emphasizing the formation of a stable 1 : 1 complex. However, in the case of Fe³⁺ nitrate, the molar conductance kept increasing with the addition of the crown

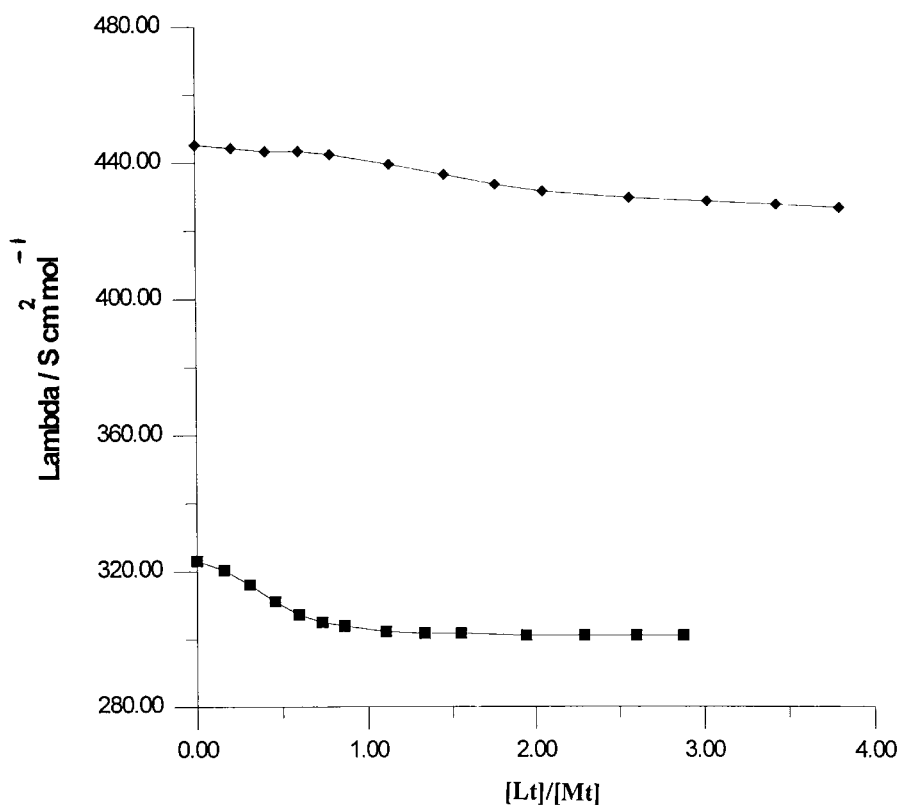


Figure 2. Molar conductance vs. $[L_T]/[M_T]$ curves for metal perchlorate crown complexes in 95% AN-H₂O mixture at 25 °C. \blacklozenge , Fe(ClO₄)₃; \blacksquare , Cu(ClO₄)₂.

ether and then begins to level off at a ratio of 2 : 1 crown-to-metal ion suggesting the formation of another complex with a ratio of 2 : 1 crown-to-metal ion. When the 80% AN-H₂O solvent mixture was used the same trend was observed as in 95% AN-H₂O but the increase in the molar conductance is smaller.

When 70% AN-H₂O solvent mixture was used the molar conductance of the nitrate salt decreased with the addition of crown ether indicating a lower mobility of the resulting metal-crown complex compared to the solvated cation. However, in this solvent mixture the molar conductance does not show any tendency of leveling off even at a mole ratio of about 3, indicating the formation of weaker complexes. The results in Table I clearly illustrate the conclusion.

It should be noted that, in the procedure of calculation of formation constants, the association between M³⁺ or M²⁺ and nitrate ion was considered negligible under the highly dilute experimental conditions used [17] and also, the calculations were done for a 1 : 1 crown-to-cation ratio for the Fe³⁺ due to the limited capability of our program.

Table I. Formation constant, enthalpies and entropies for different Phaza-15-crown-5 metal nitrate complexes in different solvent mixtures.

Salt	[MT] $\times 10^4$ mol. dm ⁻³	Solvent	20 °C	Log K_f 25 °C	30 °C	35 °C	$-\Delta H_f^\circ$ (KJ/mol)	ΔS° (J/mol K)
Cu(NO ₃) ₂	1.427	95% AN-H ₂ O	4.30 \pm 0.01	4.11 \pm 0.1	3.94 \pm 0.08	3.79 \pm 0.08	6.34 \pm 0.6	57.3 \pm 1.3
	1.157	80% AN-H ₂ O	2.97 \pm 0.05	2.81 \pm 0.04	2.66 \pm 0.03	2.52 \pm 0.03	8.31 \pm 0.7	22.3 \pm 0.8
	1.679	70% AN-H ₂ O	2.00 \pm 0.02	1.98 \pm 0.02	1.96 \pm 0.02	1.94 \pm 0.02	1.65 \pm 0.02	32.5 \pm 0.9
Fe(NO ₃) ₃ *	1.547	95% AN-H ₂ O	2.36 \pm 0.03	2.28 \pm 0.02	2.19 \pm 0.02	2.11 \pm 0.02	-28.93 \pm 1.8	143.85 \pm 3.5
	1.559	80% AN-H ₂ O	2.29 \pm 0.02	2.22 \pm 0.02	2.15 \pm 0.02	2.08 \pm 0.02	-24.84 \pm 1.6	512.2 \pm 6.8
	1.142	70% AN-H ₂ O	3.24 \pm 0.05	3.23 \pm 0.05	3.22 \pm 0.05	3.21 \pm 0.05	-4.81 \pm 0.4	78.56 \pm 2.8
Hg(NO ₃) ₂	1.343	80% AN-H ₂ O	6.66 \pm 0.15	4.66 \pm 0.10	3.30 \pm 0.07	2.36 \pm 0.05	51.85 \pm 2.3	-78.4 \pm 2.8
	1.427	95% AN-H ₂ O	4.96 \pm 0.10	4.15 \pm 0.09	3.49 \pm 0.08	2.95 \pm 0.06	25.96 \pm 1.7	-81.4 \pm 2.3
Cd(NO ₃) ₂	0.973	95% AN-H ₂ O	2.00 \pm 0.01	2.00 \pm 0.01	2.00 \pm 0.01	2.00 \pm 0.01	0.15 \pm 0.03	38.9 \pm 1.5
	1.634	80% AN-H ₂ O	2.00 \pm 0.01	2.00 \pm 0.01	2.00 \pm 0.01	2.00 \pm 0.01	0.19 \pm 0.04	38.6 \pm 1.5
	1.724	70% AN-H ₂ O	2.00 \pm 0.01	2.00 \pm 0.01	2.00 \pm 0.01	2.00 \pm 0.01	0.21 \pm 0.04	39.1 \pm 1.5

* K_f calculated for the 1 : 1 complex.

In the case of $\text{Hg}(\text{NO}_3)_2$, it was not possible to study this system in 95% AN- H_2O due to the very limited solubility of $\text{Hg}(\text{NO}_3)_2$. Therefore, this system was studied only in 80% and 70% AN- H_2O . As shown in Figure 1, the molar conductance of Hg^{2+} solution decreases with the addition of crown ether indicating a lower mobility of the complex and then begins to level off at a mole ratio of 1 : 1 crown-to-metal indicating the formation of a stable 1 : 1 complex. For the case of cadmium nitrate the addition of crown ether causes a very slight increase in molar conductivity indicating a slightly higher mobility of the cation complex compared to the solvated cation, the slope of the corresponding mole ratio plot changes at the point where the crown-to-cation mole ratio is equal to one indicating the formation of a very weak 1 : 1 crown-to-metal complex.

The plots of molar conductance of Cu^{2+} and Fe^{3+} perchlorate solution as a function of crown/metal ratio at 25 °C and in 95% AN- H_2O solvent mixture are shown in Figure 2. It is immediately obvious, that the molar conductance decreases with the addition of the crown until it reaches a molar ratio of crown-to-metal of about unity for Cu^{2+} indicating the formation of a fairly stable 1 : 1 crown to metal complex. For the ferric perchlorate system the molar conductance shows a continuous decrease with the addition of crown-ether then levels off at a ratio of 2 : 1 crown to metal indicating the formation of another complex with a ratio of 2 : 1 crown to metal. However, the formation constant was calculated for the 1 : 1 complex.

In order to achieve a better understanding of the complexation process, a thermodynamic study was conducted, where the molar conductance as a function of crown to metal was measured at various temperatures in different solvents. Examples of this study are shown in Figures 3 and 4.

Typical Vant Hoff plots of $\log K$ vs $1/T$ were obtained and the formation constants, ΔH° and ΔS° were calculated for 1 : 1 complexes and are recorded in Tables I and II. The formation constants of the complexes of PhA15C5 with metal nitrate salts in the same solvent indicate that the stability decreases in the order $\text{Hg}^{2+} > \text{Cu}^{2+} > \text{Fe}^{3+} > \text{Pd}^{2+}$. Comparing the radii of the cations Hg^{2+} 1.10 Å, Cu^{2+} 0.77 Å, Fe^{3+} 0.7 Å and Cd^{2+} 0.95 Å with the cavity size of PhA15C5 1.7–1.85 Å [4], it is obvious that although Hg^{2+} possesses a less convenient fit than Cd^{2+} for the PhA15C5 cavity, it forms the most stable complex. However, the high stability of the Hg^{2+} -PhA15C5 complexes could be due to the high soft character of Hg^{2+} [12] which results in a strong covalent interaction with the polarized nitrogen atom of the crown ether [15]. It is of interest to note that $\Delta G_{\text{solvation}}$ going from the gas phase to pure AN is: Cu^{2+} -1942, Cd^{2+} -1713 and Hg^{2+} -1717 KJ/mol [18, 19] which is in line with the complexation order $\text{Hg}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$.

The results in Table I show that $-\Delta H^\circ$ values, for Hg^{2+} complexes are higher than those of the Cu^{2+} , Fe^{3+} and Cd^{2+} complexes indicating that Hg^{2+} complexes are the most stable complexes. The fact that Hg^{2+} is weakly solvated compared to other ions will result in more exothermic complexes of Hg^{2+} . It is worth noting that ΔS for Hg^{2+} complexation is negative and does not favor complexation. Therefore,

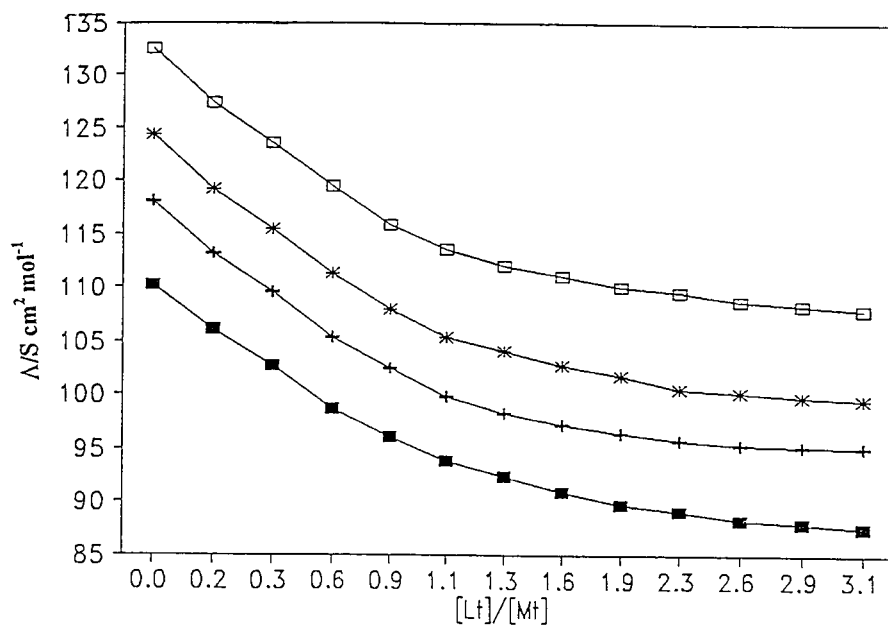


Figure 3. Molar conductance vs. $[\text{PhA15C5}]/[\text{Hg}^{+2}]$ in 80% AN- H_2O mixture at various temperatures. ■, 20 °C; +, 25 °C; *, 30 °C; □, 35 °C.

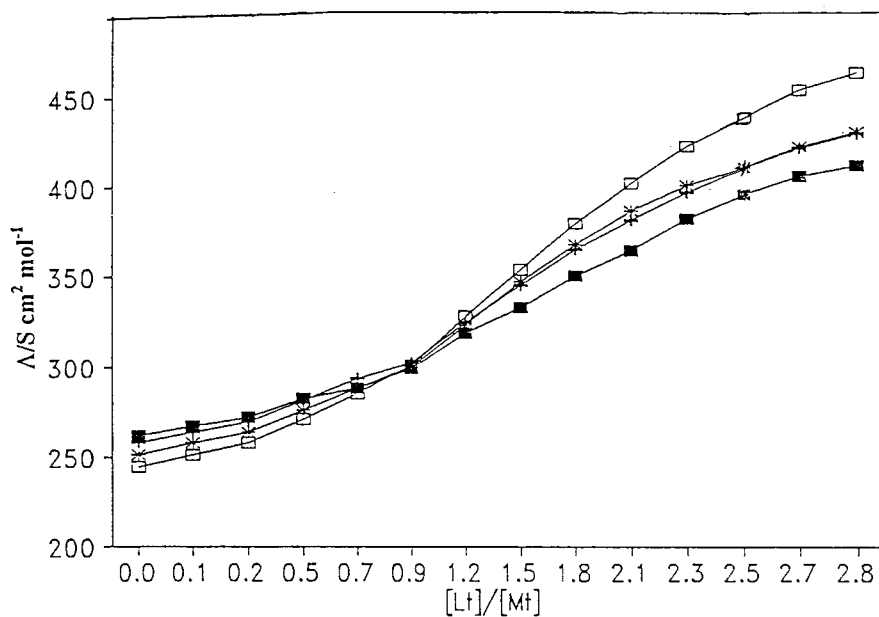


Figure 4. Molar conductance vs. $[\text{PhA15C5}]/[\text{Fe}(\text{NO}_3)_3]$ in 95% AN- H_2O mixture at various temperatures. □, 20 °C; +, 25 °C; *, 30 °C; ■, 35 °C.

Table II. Formation constants, enthalpies and entropies for different Phaza-15-crown-5 metal nitrate complexes in different solvent mixtures.

Salt	[MT] $\times 10^4$ mol. dm ⁻³	Solvent	20 °C	Log K_f 25 °C	30 °C	35 °C	$-\Delta H_f^\circ$ (KJ/mol)	ΔS° (J/mol K)
Cu(ClO ₄) ₂	1.817	95% AN-H ₂ O	5.58 \pm 0.12	5.00 \pm 0.1	4.50 \pm 0.09	4.07 \pm 0.08	15.78 \pm 1.0	42.7 \pm 1.2
	1.157	80% AN-H ₂ O	2.47 \pm 0.05	2.27 \pm 0.04	2.09 \pm 0.03	1.93 \pm 0.02	12.20 \pm 0.9	2.8 \pm 0.5
	1.015	70% AN-H ₂ O	2.35 \pm 0.04	2.18 \pm 0.03	2.03 \pm 0.02	1.89 \pm 0.02	10.70 \pm 0.8	3.86 \pm 0.6
Fe(ClO ₄) ₃ *	1.015	95% AN-H ₂ O	2.05 \pm 0.04	2.31 \pm 0.06	2.56 \pm 0.05	2.81 \pm 0.05	87.00 \pm 2.3	-244.4 \pm 5.6
	0.736	80% AN-H ₂ O	2.21 \pm 0.05	2.33 \pm 0.06	2.44 \pm 0.04	2.55 \pm 0.04	39.14 \pm 1.8	-67.3 \pm 1.6
	1.220	70% AN-H ₂ O	3.24 \pm 0.06	3.36 \pm 0.07	3.48 \pm 0.08	3.59 \pm 0.05	40.20 \pm 1.8	-71.7 \pm 1.7

* K_f calculated for the 1 : 1 complex.

the complexation is due to an enthalpic origin. For the Cu^{2+} complexation both ΔH° and ΔS° favor the formation of the complex and the value of ΔH° predicts less stable complexes than those of Hg^{2+} .

The ferric nitrate system shows opposite behavior where ΔH° is positive thus destabilizing the complex and ΔS is positive which stabilizes the complex. As a result this complex is relatively unstable and transforms into another complex with a ratio of 2 : 1 crown to metal cation. As shown from Figure 4 it is easily predicted that ΔH for the second complex is negative thus favouring the complexing process.

The thermodynamic data in Tables I and II illustrate that the enthalpy and entropy changes obtained for different metal ion crown complexes vary with the solvent mixture composition. As can be seen, except with ferric nitrate, the complexes are enthalpy stabilized and with the exception of ferric perchlorate and mercuric nitrate are entropy stabilized. It should be noted that similar thermodynamic behaviors were previously reported for most of the macrocyclic complexes studied in mixed solvents [20]. The entropy change of the metal ion crown-system upon complexation has been related to some factors such as the change in the conformational entropy of the ligand and the crown cavity size, the extent of crown-solvent interaction and the difference in the solvation of the free and complexed cation. From the data in Tables I and II it is clearly obvious that in most cases, the enthalpy changes shift to more negative values by increasing the amount of AN in the AN- H_2O mixture. This behaviour is most probably due to the decreased competition of the solvent mixture with crown molecules for the cation.

Examination of Tables I and II reveals that the anion has an effect on the conductance behavior and on the complexation stability. As an example in 95% AN- H_2O solvent mixture, replacing the nitrate by perchlorate increases $\log K_f$ for the copper complexes from 4.11 to 5.00. The same trend was also observed for Fe^{3+} complexes but with less effect. This behavior could be explained as follows, since the perchlorate ion has a larger radius (2.36 Å) compared to the nitrate ion (1.89 Å), the perchlorate stabilized the electron density more than the nitrate, which makes the nitrate more nucleophilic, as a result the metal-crown interaction is weakened.

The data in Tables I and II clearly illustrate the fundamental influence of the solvent properties on the stability of transition metal-PhA15C5 complexes. The formation constants for a given complex increases with increasing weight percent of acetonitrile in the mixed solvent. It is well known that the solvating ability of the solvent, as expressed by the Gutmann donor number plays an important role in different complexation processes. It is expected that AN, with a low donor number (DN = 14.1), will increase the stability of the complexes. For mercury nitrate, copper perchlorate and nitrate, it is obvious that the formation constants for a given complex increases with increasing weight percent of acetonitrile in the mixed solvent.

For the cadmium nitrate-crown system, the stability of the complexes are almost the same in the three solvent mixtures, indicating that the solvation of cadmium cation is the same.

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