

Study of Complex Formation between *N*-Phenylaza-15-Crown-5 with Mg^{2+} , Ca^{2+} , Ag^+ and Cd^{2+} Metal Cations in Some Binary Mixed Aqueous and Non-aqueous Solvents Using the Conductometric Method

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Abstract

The complexation reactions between Mg^{2+} , Ca^{2+} , Ag^+ and Cd^{2+} metal cations with *N*-phenylaza-15-crown-5 (Ph-N15C5) were studied in acetonitrile (AN)–methanol (MeOH), methanol (MeOH)–water (H_2O) and propanol (PrOH)–water (H_2O) binary mixtures at different temperatures using the conductometric method. The conductance data show that the stoichiometry of all of the complexes with Mg^{2+} , Ca^{2+} , Ag^+ and Cd^{2+} cations is 1:1 (L:M). The stability of the complexes is sensitive to the solvent composition and a non-linear behaviour was observed for variation of $\log K_f$ of the complexes versus the composition of the binary mixed solvents. The selectivity order of Ph-N15C5 for the metal cations in neat MeOH is $Ag^+ > Cd^{2+} > Ca^{2+} > Mg^{2+}$, but in the case of neat AN is $Ca^{2+} > Cd^{2+} > Mg^{2+} > Ag^+$. The values of thermodynamic parameters (ΔH_c° , ΔS_c°) for formation of Ph-N15C5– Mg^{2+} , Ph-N15C5– Ca^{2+} , Ph-N15C5– Ag^+ and Ph-N15C5– Cd^{2+} complexes were obtained from temperature dependence of stability constants and the results show that the thermodynamics of complexation reactions is affected by the nature and composition of the mixed solvents.

Introduction

The first macrocyclic polyethers were reported by Luttringhaus in 1937 [1]. However, the importance of these compounds began from 1967 with the synthesis of dibenzo-18-crown-6 (DB18C6) by Pedersen and the observation that this compound and its homologues form very strong complexes with alkali and alkaline earth metal cations [2]. The values of stability constants as well as the values of enthalpy changes (ΔH_c°), entropy changes (ΔS_c°) and the heat capacity changes (ΔC_p) of various crown ether complexes are summarized in two reviews by Christensen *et al.* [3, 4].

An important part of cyclic polyethers chemistry deals with the alkali and alkaline earth metal ion complexes because of the vital role of these cations in biological systems [5]. Naturally occurring macrocycles were shown to be capable of activity transport metal cations through the biological membranes. Macrocyclic crown ethers which are similar to antibiotic in ion transport through membranes in biological systems

[6], can be used as models for study of biological systems.

A considerable research has been carried out in a wide range of applications of these compounds in different areas such as organic synthesis [7], polymer synthesis [8], separation of metal ions [9, 10], construction of ion-selective electrodes [11, 12], chemical analysis [13], use of optically active crown compounds for the resolution of D, L-amino acids [14], as enzyme models, biophysics, medicine [15] and agrochemicals.

The widespread use of non-aqueous solvents began 1950s in various field of pure and applied chemistry and has contributed greatly to later advances in chemical sciences and technologies [16]. Non-aqueous solvents are often mix with water or some other organic solvents, in order to obtain desirable solvent properties.

Studies of crown ether complexes in various solvents, show that the thermodynamic and kinetic parameters for complexation processes are affected by the nature and composition of the solvent system [17, 18]. The goal of the present investigation is to study the effect of the nature of the cation, especially the solvent properties on complexation reactions of Ph-N15C5 complexes with Mg^{2+} , Ca^{2+} , Ag^+ and Cd^{2+} metal cations in AN–MeOH,

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MeOH–H₂O and PrOH–H₂O binary systems using the conductometric technique.

Experimental

Reagents and solvents

Ph-N15C5 (Merck), argent nitrate (Merck), cadmium nitrate (Riedel), magnesium nitrate (BDH) and calcium nitrate (Merck) were used without further purification. Acetonitrile (Merck), methanol (Merck), propanol (Riedel) with the highest purity and triplet distilled water were used as solvents.

The experimental procedure to obtain the formation constants of complexes was as follows: a solution of metal salt (5×10^{-4} M) 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 (2.5×10^{-3} M) 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.

Apparatus

The conductance measurements were performed on a digital AMEL conductivity apparatus, model 60, in a water bath thermostated at a constant temperature which maintained within ± 0.03 °C. The electrolytic conductance was measured using a cell consisting of two platinum electrodes to which an alternating potential was applied. A conductometric cell with a cell constant of 0.79 cm^{-1} was used throughout the studies.

Results

The variation of molar conductance (Λ_m) versus the ligand to the cation molar ratio ($[L]_t/[M]_t$) for complexation of Ph-N15C5 with Mg^{2+} , Ca^{2+} , Ag^+ and Cd^{2+} cations in AN–MeOH, MeOH–H₂O and PrOH–H₂O binary systems were studied at different temperatures. Three typical series of molar conductance values as a function of ligand/metal cation mole ratio plots in MeOH–H₂O (mol% MeOH = 25) binary systems and in pure PrOH and pure AN are shown in Figures 1–3, respectively.

The stability constants of the Ph-N15C5 crown ether complexes at each temperature were calculated from the variation of in the molar conductance as a function of ligand/metal cation mole ratios using a GENPLOT computer program [19]. The details of the calculation of the stability constants of complexes by conductometric method has been described elsewhere [20]. The values of stability constants ($\log K_f$) for Ph-N15C5– M^{n+} ($\text{M}^{n+} = \text{Mg}^{2+}$, Ca^{2+} , Ag^+ and Cd^{2+}) complexes

in various solvent systems are listed Tables 1 and 2. The van't Hoff plots of $\log K_f$ versus $1/T$ for all of investigated systems were constructed. The changes in standard enthalpy (ΔH_c°) were obtained from the slope of the van't Hoff plots and the changes in standard entropy (ΔS_c°) were calculated from the relationship $\Delta G_{c,298.15}^\circ = \Delta H_c^\circ - 298.15\Delta S_c^\circ$. The thermodynamic data are summarized in Tables 3 and 4.

The variations of $\log K_f$ versus the mole fraction of MeOH for Ph-N15C5– Ca^{2+} complex in AN–MeOH and for Ph-N15C5– Ag^+ complex in MeOH–H₂O binary systems at different temperatures are shown in Figures 4 and 5, respectively, and the variations of the stability constants ($\log K_f$) of Ph-N15C5– Mg^{2+} , Ph-N15C5– Ca^{2+} , Ph-N15C5– Ag^+ and Ph-N15C5– Cd^{2+} complexes as a function of cationic radii in various AN–MeOH binary systems are shown in Figure 6.

Discussion

As seen from Figure 1, addition of Ph-N15C5 to a solution of Ag^+ cation in MeOH–H₂O (mol% MeOH = 25) binary systems at different temperatures results in a decrease in molar conductivity which indicates that the Ph-N15C5– Ag^+ complex in this solution is less mobile than free solvated Ag^+ cation, but as seen from Figures 2 and 3, addition of Ph-N15C5 to Ag^+ and Ca^{2+} cations in pure PrOH and pure AN solutions at different temperatures results in an increase in molar conductivity which indicates that the Ph-N15C5– Ag^+ and Ph-N15C5– Ca^{2+} complexes in pure PrOH and pure AN are more mobile than free solvated Ag^+ and Ca^{2+} cations. The slope of the corresponding molar conductivity versus ligand/metal cation plots changes at the point where the ligand to cation mole ratio is about 1, which is an evidence for formation of a relatively stable

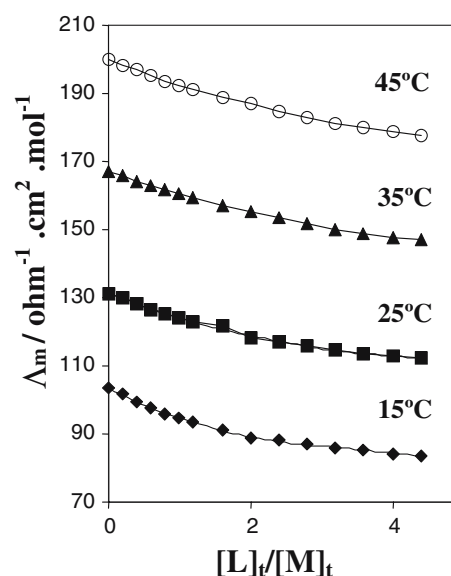


Figure 1. Molar conductance–mole ratio plots for the Ph-N15C5– Ag^+ complex in MeOH–H₂O (mol% MeOH = 25) binary system at different temperatures.

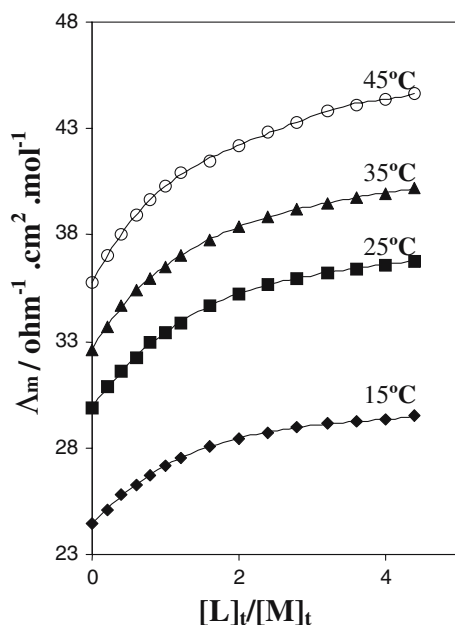


Figure 2. Molar conductance–mole ratio plots for the Ph-N15C5–Ag⁺ complex in pure PrOH at different temperatures.

1:1 complex. As is shown in Figures 1–3, the curvature of the plots of the Ph-N15C5–Ag⁺ and Ph-N15C5–Ca²⁺ complexes decreases as the temperature increases which is an evidence for formation of a weaker complex at higher temperatures, therefore, there is an exothermic reaction between Ag⁺ and Ca²⁺ cations with Ph-N15C5 in MeOH–H₂O binary mixture and in pure AN and pure PrOH. Similar behaviour was observed for the Ph-N15C5–Mg²⁺ and Ph-N15C5–Cd²⁺ complexes in pure acetonitrile, but in the case of the Ph-N15C5–Ag⁺ complex in PrOH–H₂O binary systems, the stability

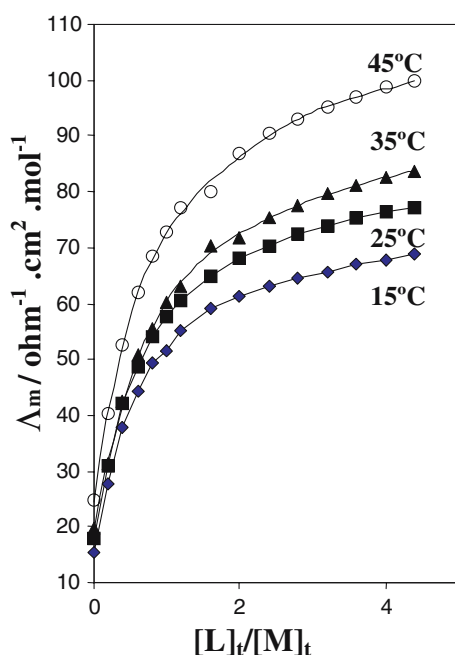


Figure 3. Molar conductance–mole ratio plots for the Ph-N15C5–Ca²⁺ complex in pure AN at different temperatures.

constant increases with increasing the temperature which shows that the complexation reaction between Ag⁺ cation and Ph-N15C5 in these solvent systems is endothermic.

As seen from Table 1, in all cases, as the concentration of AN is increased in AN–MeOH binary mixtures, the stability of the complexes increases. These results seem reasonable, since in methanol with a relatively high Gutmann Donor Number (DN=20), the solvation of the cations should be stronger than acetonitrile with lower solvating ability (DN=14).

The data in Table 2, show that as the concentration of water is increased in MeOH–H₂O and PrOH–H₂O binary mixtures, the stability of complexes decreases. In a strong solvating solvent such as H₂O with a relatively high Gutmann Donor Number (DN=33), the solvation of metal cation and possibly of the ligand should be stronger than solvents of lower solvating abilities such as methanol (DN=20) and propanol (DN=18). Therefore, the stabilities of crown ether complexes increase as the concentration of water is lowered in the mixed binary systems.

The thermodynamic parameters for complex formation are given in Tables 3 and 4. The enthalpy and entropy values for the complexation reactions vary with the nature and composition of the mixed solvents and the experimental values of ΔH_c° and ΔS_c° show that in some cases, the complexes are enthalpy stabilized but entropy destabilized. As expected, the values of ΔH_c° and ΔS_c° depend strongly on the nature of the medium. The value and the sign of the standard entropy changes are expected to vary with different parameter, such as changes in flexibility of the macrocyclic ligands during the complexation processes and the extent of cation-solvent, crown ether-solvent and complex-solvent interactions [21, 22].

As is shown in Figures 4 and 5, the variation of the stability constants of the Ph-N15C5–Mⁿ⁺ (Mⁿ⁺ = Mg²⁺, Ca²⁺, Ag⁺, Cd²⁺) complexes versus the solvent composition in AN–MeOH and MeOH–H₂O binary systems, is not linear. Similar behaviour has been observed for the 18C6–Hg²⁺, 18C6–Ag⁺ and 15C5–Mg²⁺ complexes in AN–MeOH binary systems [23, 24]. This behaviour may be related to changes occurring in the structure of the solvent mixtures and, therefore, changing in the solvation properties of the cyclic polyether, cations and even complexes in these solvent mixtures. Some structural changes probably occur in the structure of the solvents when they mix with one another. These structural changes may result in changing the interactions of those solvents with the solutes. In addition, the heteroselective solvation of the cation, anion and ligand and the character of its changes with the composition of the mixed solvents and temperature may be effective in these complexation processes. Parasad and co-workers have studied the interactions between acetonitrile and methanol molecules by excess adiabatic compressibility (β^E) and excess intermolecular free length (L_r^E) measurements at

Table 1. Log K_f values of Ph-N15C5-Mg²⁺, Ph-N15C5-Ca²⁺, Ph-N15C5-Ag⁺ and Ph-N15C5-Cd²⁺ complexes in AN-MeOH binary mixtures at different temperatures

Medium	log $K_f \pm SD^a$			
	15 °C	25 °C	35 °C	45 °C
<i>Ph-N15C5-Mg²⁺</i>				
Pure AN	3.02 ± 0.03	2.95 ± 0.03	2.94 ± 0.06	2.93 ± 0.08
75% AN-25%MeOH ^b	1.7 ± 0.3	1.8 ± 0.2	1.9 ± 0.3	1.8 ± 0.3
50% AN-50%MeOH	– ^d	2.1 ± 0.2	D	D
25% AN-75%MeOH	– ^d	d	D	D
Pure MeOH	< 1	< 1	< 1	D
<i>Ph-N15C5-Ca²⁺</i>				
Pure AN	4.0 ± 0.1	3.95 ± 0.09	3.82 ± 0.01	3.80 ± 0.07
75% AN-25% MeOH ^b	1.0 ± 0.1	1.1 ± 0.2	1.3 ± 0.2	1.8 ± 0.3
50% AN-50%MeOH	1.7 ± 0.3	1.8 ± 0.3	1.8 ± 0.2	2.01 ± 0.09
25% AN-75% MeOH	D	d	D	d
Pure MeOH	1.0 ± 0.3	1.2 ± 0.3	1.3 ± 0.3	d
<i>Ph-N15C5-Ag⁺</i>				
Pure AN	1.8 ± 0.3	1.7 ± 0.3	1.2 ± 0.2	1.1 ± 0.2
75% AN-25%MeOH ^b	– ^d	– ^d	– ^d	– ^d
50% AN-50% MeOH	– ^d	1.28 ± 0.09	1.79 ± 0.03	2.0 ± 0.3
25% AN-75%MeOH	– ^d	– ^d	– ^d	– ^d
Pure MeOH	3.690 ± 0.005	3.67 ± 0.02	3.6 ± 0.1	3.50 ± 0.02
<i>Ph-N15C5-Cd²⁺</i>				
Pure AN	3.60 ± 0.05	3.54 ± 0.05	3.66 ± 0.08	3.50 ± 0.05
75%AN-25% MeOH ^b	2.4 ± 0.2	2.20 ± 0.08	1.9 ± 0.1	1.4 ± 0.3
50%AN-50%MeOH	1.7 ± 0.2	1.9 ± 0.2	1.9 ± 0.2	2.2 ± 0.1
25%AN-75%MeOH	– ^d	– ^d	– ^d	– ^d
Pure MeOH	2.23 ± 0.3	2.3 ± 0.1	2.60 ± 0.098	–

^aSD = standard deviation.

^bComposition of binary mixtures is expressed in mol% for each solvent system.

^cThe concentration of each metal cation was 5×10^{-4} M.

^dSD of log K_f is high.

303.15 K and they showed that these parameters become increasingly negative with increasing strength of interaction between the component molecules [25]. In addition, it has been shown that there is an interaction

between acetonitrile and methanol molecule ($K_{\text{ass.}} = 1.23$) via hydrogen bonding in their binary mixtures [26].

The changes of log K_f of the Ph-N15C5-Mg²⁺, Ph-N15C5-Ca²⁺, Ph-N15C5-Ag⁺ and Ph-N15C5-Cd²⁺

Table 2. Log K_f values of Ph-N15C5-Ag⁺ complexes in MeOH-H₂O and PrOH-H₂O binary mixtures at different temperatures

Medium	log $K_f \pm SD^a$			
	15 °C	25 °C	35 °C	45 °C
<i>Ph-N15C5-Ag⁺</i>				
Pure MeOH	3.690 ± 0.005	3.67 ± 0.02	3.6 ± 0.1	3.50 ± 0.02
75% MeOH-25%H ₂ O ^b	3.68 ± 0.03	3.66 ± 0.07	3.40 ± 0.01	3.28 ± 0.05
50% MeOH-50%H ₂ O	3.47 ± 0.04	3.10 ± 0.02	2.98 ± 0.02	2.73 ± 0.04
25% MeOH-75%H ₂ O	3.19 ± 0.06	2.90 ± 0.06	2.62 ± 0.04	2.58 ± 0.03
<i>Pure H₂O</i>				
<i>Ph-N15C5-Ag⁺</i>	d	d	d	d
Pure PrOH	3.56 ± 0.01	3.418 ± 0.00	3.397 ± 0.00	3.32 ± 0.05
75% PrOH-25%H ₂ O ^b	2.6 ± 0.4	2.9 ± 0.4	3.1 ± 0.1	2.80 ± 0.06
50% PrOH-50%H ₂ O	2.0 ± 0.2	2.87 ± 0.08	2.4 ± 0.1	3.16 ± 0.01
25% PrOH-75%H ₂ O	2.36 ± 0.09	2.40 ± 0.08	2.44 ± 0.05	2.0 ± 0.2
Pure H ₂ O	d	d	d	d

^aSD = standard deviation.

^bComposition of binary mixtures is expressed in mol% for each solvent system.

^cThe concentration of each metal cation was 5×10^{-4} M.

^dCrown ether is not dissolved.

Table 3. Thermodynamic parameters for formation of Ph-N15C5–Mg²⁺, Ph-N15C5–Ca²⁺, Ph-N15C5–Ag⁺ and Ph-N15C5–Cd²⁺ complexes in AN–MeOH binary mixtures

Medium	log $K_f \pm SD^a$ (25 °C)	$-\Delta G_c^\circ \pm SD^a$ (kJ/mol)	$\Delta H_c^\circ \pm SD^a$ (kJ/mol)	$\Delta S_c^\circ \pm SD^a$ (J/mol K)
<i>Ph-N15C5–Mg²⁺</i> ^c				
Pure AN	2.95 ± 0.03	16.8 ± 0.2	–5 ± 2	40 ± 7
75%AN–25% MeOH ^b	1.8 ± 0.4	10.3 ± 0.2	16.54 ± 0.04	90 ± 7
<i>Ph-N15C5–Ca²⁺</i> ^c				
Pure AN	3.95 ± 0.09	22.5 ± 0.5	–12 ± 2	35 ± 6
75%AN–25%MeOH ^b	1.1 ± 0.2	6 ± 1	44 ± 12	168 ± 40
50%AN–50%MeOH	1.8 ± 0.3	10 ± 2	18.3 ± 0.8	95 ± 6
25%AN–75%MeOH	1.2 ± 0.3	7 ± 2	25 ± 4	107 ± 11
Pure MeOH	1.4 ± 0.3	8 ± 2	31 ± 5	131 ± 15
<i>Ph-N15C5–Ag⁺</i> ^c				
Pure AN	1.70 ± 0.3	9.7 ± 0.3	–45 ± 10	118 ± 29
50%AN–50%MeOH ^b	1.28 ± 0.09	7.30 ± 0.04	1.0 ± 0.2	–21.1 ± 0.6
Pure MeOH	3.67 ± 0.02	20.9 ± 0.3	–11 ± 2	33 ± 7
<i>Ph-N15C5–Cd²⁺</i> ^c				
Pure AN	3.54 ± 0.05	20.2 ± 0.3	–6 ± 2	48 ± 13
75%AN–50%MeOH ^d	2.20 ± 0.08	12.6 ± 0.4	–58 ± 8	152 ± 27
50%AN–50%MeOH	1.9 ± 0.2	11 ± 1	26 ± 7	–91 ± 23
Pure MeOH	2.33 ± 0.1	13.3 ± 0.6	31 ± 9	–149 ± 30

^aSD = standard deviation.

^bComposition of binary mixtures is expressed in mol% for each solvent system.

^cThe concentration of each metal cation was 5 × 10^{–4} M.

Table 4. Thermodynamic parameters for Ph-N15C5–Ag⁺ complex in MeOH–H₂O and PrOH–H₂O binary mixtures

Medium	log $K_f \pm SD^a$ (25 °C)	$-\Delta G_c^\circ \pm SD$ (kJ/mol)	$\Delta H_c^\circ \pm SD^a$ (kJ/mol)	$\Delta S_c^\circ \pm SD^a$ (J/mol K)
<i>Ph-N15C5–Ag⁺</i> ^c				
Pure MeOH	3.67 ± 0.02	20.9 ± 0.1	–11 ± 2	33 ± 7
75%MeOH–25%H ₂ O ^b	3.66 ± 0.07	20.9 ± 0.4	–25 ± 6	– ^d
50%MeOH–50%H ₂ O	3.10 ± 0.02	17.7 ± 0.1	–41 ± 5	–78 ± 17
25%MeOH–50%H ₂ O	2.90 ± 0.06	16.6 ± 0.3	–37 ± 6	–68 ± 20
<i>Ph-N15C5–Ag⁺</i> ^c				
Pure PrOH	3.418 ± 0.008	19.50 ± 0.04	–13 ± 2	22 ± 7
75% PrOH–25%H ₂ O ^b	2.9 ± 0.4	16.6 ± 0.5	45 ± 2	207 ± 6
50%PrOH–50%H ₂ O	2.87 ± 0.08	16.4 ± 0.4	63 ± 3	266 ± 10
25%PrOH–75%H ₂ O	2.40 ± 0.08	13.7 ± 0.4	45 ± 2	206 ± 6
Pure H ₂ O	e	e	e	e

^aSD = standard deviation.

^bComposition of binary mixtures is expressed in mol% for each solvent system.

^cThe concentration of each metal cation was 5 × 10^{–4} M.

^dSD of log K_f is high.

^eCrown ether is not dissolved.

complexes *versus* the ionic radii in various AN–MeOH binary mixtures is shown in Figure 6. Some reversals of stability can be observed which show that the selectivity order of the ligand for these metal cations is affected by the nature and composition of the solvent systems. The Ph-N15C5–Cd²⁺ complex is more stable compared to the other complexes in 75–25 mol% AN–MeOH binary mixture with respect to the other solvent systems.

The order of stability of complexes formed between Ph-N15C5 and these metal cations in pure MeOH is

Ag⁺ > Cd²⁺ > Ca²⁺ > Mg²⁺. The Ag⁺ cation forms a more stable complex with Ph-N15C5 than the other three cations. Although the ionic radius size of Ag⁺ cation (1.26 Å) is bigger than the size of the Ph-N15C5 cavity (1.7–2.2 Å) [27], but since the Ag⁺ cation is a softer acid than Mg²⁺, Ca²⁺ and Cd²⁺ cations [28], therefore, the interaction of the Ag⁺ cation with the nitrogen atom of Ph-N15C5 ligand is stronger than Mg²⁺, Ca²⁺ and Cd²⁺ cations. The Ag⁺ cation may also interact with the pi electron system of the aromatic substituent present in the macrocyclic ligand. It is interesting to note that,

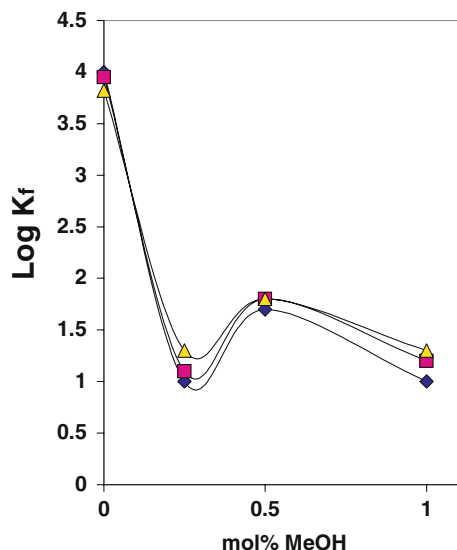


Figure 4. Variation of the stability constant of Ph-N15C5-Ca²⁺ with the composition of the AN-MeOH binary systems at different temperatures: 15 °C (◆), 25 °C (□) and 35 °C (△).

the order of stability of complexes formed between Ph-N15C5 and these metal cations in pure AN is Ca²⁺ > Cd²⁺ > Mg²⁺ > Ag⁺. Therefore, a reversal in selectivity is observed in pure acetonitrile compared to the methanol solutions. Since the Ag⁺ cation is a soft acid, therefore, it is strongly solvated by acetonitrile molecules via its nitrogen atom as a soft base [27], therefore, it forms a weaker complex compared to the other metal cations. The results obtained in this study show that the selection of solvents as mixture components and their concentration may create possibilities to change the properties of the solvent system in a desired direction.

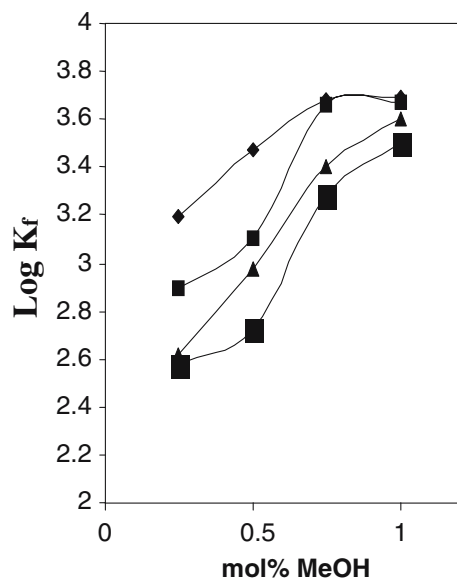


Figure 5. Variation of the stability constant of Ph-N15C5-Ag⁺ with the composition of the MeOH-H₂O binary systems at different temperatures: 15 °C (◆), 25 °C (■), 35 °C (▲) and 45 °C (■).

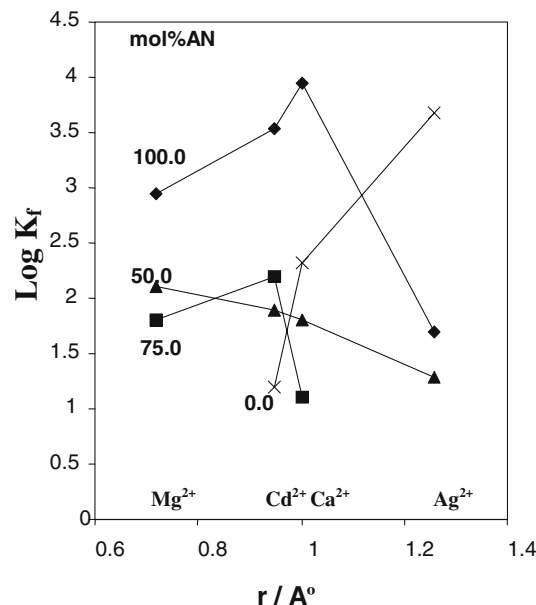


Figure 6. Variation of log K_f for Ph-N15C5-Mg²⁺, Ph-N15C5-Ca²⁺, Ph-N15C5-Ag⁺ and Ph-N15C5-Cd²⁺ complexes versus cationic radii in AN-MeOH binary solvent systems at 25 °C.

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