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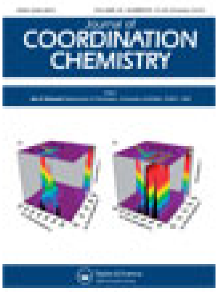

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Complexing ability of kryptofix5 with Ag^+ in some binary mixed solvents at different temperatures

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The stability constant ($\log K_f$) for complexation of 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (kryptofix5) with Ag^+ has been determined conductometrically in acetonitrile–ethyl acetate (AN–EtOAc), methanol–ethyl acetate (MeOH–EtOAc), methanol–water (MeOH–H_2O) and dimethyl sulfoxide–ethyl acetate (DMSO–EtOAc) solutions at different temperatures . A 1 : 1 [ML] complex was formed between the metal cation and ligand in most solvent systems. The stability constant of the resulting 1 : 1 complex was determined from computer fitting of the conductance–mole ratio data. The stability order of the $(\text{kryptofix5.Ag})^+$ complex in the studied binary mixed solvent solutions at 25°C was found to be MeOH–EtOAc > AN–EtOAc > DMSO–EtOAc. The results show that in some cases the stoichiometry of the complex formed between Ag^+ and the ligand changes with the nature of the solvent and that solvation numbers of the metal cation and the resulting complexes change with temperature. The values of the standard thermodynamic parameters (ΔH_c^0, ΔS_c^0) show that in all cases the $(\text{kryptofix5.Ag})^+$ complex is entropy stabilized, but the enthalpy, depending on solvent system, is stabilizing or destabilizing.

Keywords: Ag^+; 1,13-Bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane; Mixed solvents; Conductometry

1. Introduction

Kryptofix5 (scheme 1) is a quinoline-terminated podand which was investigated by Vögtle and Weber in 1979 whose early work involved synthesis of podands, which are able to form stable crystalline compounds with a wide variety of alkali metal salts as well as transition metal cations [1, 2]. Podands are open-chain hosts, whose specific cation selectivity and other properties make them useful to compare to crown ethers [3–5]. Sometimes the flexible nature of these acyclic crown ethers permit conformational changes in the binding and releasing process, such as liquid–liquid extraction [6, 7] and membrane transport experiments [8, 9]. Podands generally have flexibility on binding a guest and the conformational change that occurs produces a stable host–guest complex which may result in allosteric effects if podands are capable of binding more than one guest [10]. These open-chain crown types with aromatic end groups wrap themselves

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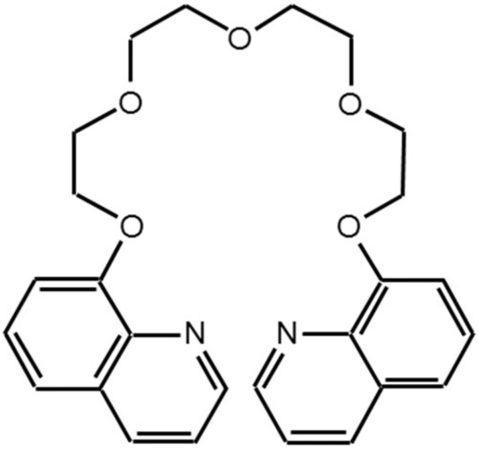

Scheme 1. Structure of 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (kryptofix5).

around the cations in a helical manner to make a pseudo-cycle [11]. As a podand, kryptofix5 has two donor centers, the lone pair of electrons on nitrogen in the quinoline ring and the π system in the aromatic ring [12]. Ag^+ is a strong acid for nitrogen atoms, but also an electrostatic ion for oxygen atoms [13–15]. The bond energy for O–Ag^+ is known as $6\,kJ\,mol^{-1}$ in methanol [10].

With high cation selectivities, numerous thermodynamic data on complexation of crown ethers [16–20] are available while thermodynamic [21–23] and structural [24] studies for complexation of podands in solution have not been examined intensively. Podands have applications in many areas, such as construction of modified carbon paste electrode [25], phase transfer catalysis [26], and as a carrier through a supported liquid membrane [27]. Also they have been used for potentiometric detection of organic acids [28]. These applications have generated interest in podand–metal ion complexes.

In solvent mixtures, selective solvation of a cation by only one solvent component has been reported [29, 30]. Therefore, the choice of solvent can have significant consequences on binding of a guest. Polar solvents interact electrostatically with the host molecules. Such solvents substantially decrease binding of the charged species, as the solvent dipole can interact strongly with a charged center, thus making the solvent–host or solvent–guest interactions harder to break. Other solvents are able to disrupt the binding by electron-pair donor and hydrogen-bond acceptor interactions [31].

In order to achieve appropriate solvent properties, we use a mixture of two solvents. The physicochemical properties of mixed solvents are important from a theoretical and practical point of view, because many chemical and electrochemical reactions might be carried out in such media. The solvating ability of solvents in their mixtures can be different from those of neat media. The effect of mixed solvent properties on formation of podand–metal cation complexes is of interest because solvation capacities of podand molecules and cations change on changing the mixed solvent composition. On the other hand, the species are solvated competitively by the solvents. The formation of crown ether complexes with various metal cations in aqueous and pure non-aqueous solvents have been extensively reported in the literature, and also recent studies have been carried out in some mixed solvent solutions [32], but the complexation reaction of acyclic crown ethers in mixed solvent systems have been investigated only to a very limited extent.

Formation constants of metal cation complexes can be measured by conductometry with high precision, especially for weak or medium strength interactions at extremely low concentrations in solutions, where the interactions between the metal cations and anions are very small. In principle, measurements of the variation of electrical conductance with concentration of metal salts and receptors can determine the strength, stoichiometry, and stability constant of complex formation, and assess the nature of the interactions taking place in solution.

With the aim of studying the effect of the nature of the solvent system and influence of temperature on complexation of kryptofix5 with Ag^+, we report the results obtained for the stoichiometry, stability and also the thermodynamic parameters for formation of the $(kryptofix5.Ag)^+$ complex in acetonitrile (AN), ethyl acetate (EtOAc), methanol (MeOH), water (H_2O), and dimethyl sulfoxide (DMSO) and in their binary mixtures at different temperatures using conductometry.

2. Experimental

2.1. *Reagents and procedure*

1,13-Bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (kryptofix5) and $AgNO_3$ were purchased from Merck (>99% purity) and used without purification. Ethyl acetate, methanol, acetonitrile, and dimethyl sulfoxide all from Merck of the highest purity and doubly distilled water were used as solvents. The experimental procedure to obtain the stability constant of the $(kryptofix5.Ag)^+$ complex is as follows: a solution of silver(I) salt ($1.0 \times 10^{-4}\,mol\,L^{-1}$) was placed in a titration cell and the conductance of the solution was measured, then a step-by-step increase of the ligand solution prepared in the same solvent ($2.0 \times 10^{-3}\,mol\,L^{-1}$) was carried out using a pre-calibrated micropipette. In order to keep the electrolyte concentration constant during the titration, both the starting solution and the titrant had the same metal ion concentration.

2.2. *Apparatus*

Conductance measurements were performed on a digital conductometer Jenway, model 4510, at a frequency of 1 kHz using a specially designed water jacketed cell (150 mL, pyrex) equipped with a magnetic stirrer and connected to a thermostated circulating water bath (LAUDA) with a precision of ±0.1°C equipped with a refrigerating unit.

2.3. *Theoretical calculations*

Formation of a 1 : 1 complex between a solvated metal cation, M^{n+}, and a ligand, L, can be described as the following equilibrium:

$$M^{n+} + L \leftrightarrow ML^{n+}. \tag{1}$$

The corresponding equilibrium constant, K_f, is given by

$$K_f = \frac{[\mathrm{ML}^{n+}]}{[\mathrm{M}^{n+}][\mathrm{L}]} \times \frac{f\mathrm{ML}^{n+}}{f\mathrm{M}^{n+} f\mathrm{L}}, \tag{2}$$

where $[\mathrm{ML}^{n+}]$, $[\mathrm{M}^{n+}]$, [L], and f represent the equilibrium molar concentrations of the complex, free cation, free ligand, and the activity coefficient of the species indicated, respectively [6]. In this article, L = kryptofix5 and $\mathrm{M}^{n+} = \mathrm{Ag}^+$. Under dilute conditions, where the ionic strength is less than $0.001\,\mathrm{mol\,L^{-1}}$, which was employed in these experiments, the $f^{n+}_{\mathrm{ML}}/f^{n+}_{\mathrm{M}}\ f_{\mathrm{L}}$ factor can be reasonably assumed to be unity and, therefore, the equilibrium constant obtained in this study is the thermodynamic equilibrium constant.

The mass balance equation of an ML^{n+} type complex (equations (3) and (4)) used in the computer program (GENPLOT) should be solved in order to obtain equation (5) for the free ligand concentration [L].

$$C_{\mathrm{M}} = [\mathrm{M}^{n+}] + [\mathrm{ML}^{n+}], \tag{3}$$

$$C_{\mathrm{L}} = [\mathrm{L}] + [\mathrm{ML}^{n+}]. \tag{4}$$

Substitution of equations (3) and (4) into equation (2) and rearrangement yields:

$$K_f[\mathrm{L}]^2 + (1 + K_f(C_{\mathrm{M}} - C_{\mathrm{L}}))[\mathrm{L}] - C_{\mathrm{L}} = 0. \tag{5}$$

The complex-formation constant in terms of the molar conductance can be expressed as

$$K_f = \frac{[\mathrm{ML}^{n+}]}{[\mathrm{M}^{n+}][\mathrm{L}]} = \frac{(\Lambda_{\mathrm{M}} - \Lambda_{\mathrm{obs}})}{(\Lambda_{\mathrm{obs}} - \Lambda_{\mathrm{ML}})[\mathrm{L}]}, \tag{6}$$

where

$$[\mathrm{L}] = C_{\mathrm{L}} - \frac{C_{\mathrm{M}}(\Lambda_{\mathrm{M}} - \Lambda_{\mathrm{obs}})}{(\Lambda_{\mathrm{M}} - \Lambda_{\mathrm{ML}})}. \tag{7}$$

Here, Λ_{M} is the molar conductance of the metal nitrate before addition of the ligand, Λ_{obs} the molar conductance of the solution during titration, and Λ_{ML} the molar conductance of the complexed ion. C_{L} is the analytical concentration of the ligand added and C_{M} is the analytical concentration of the metal nitrate. The stability constant of the complex at each temperature was obtained from computer fitting of equations (6) and (7) to the molar conductance–mole ratio data using a non-linear least squares program, GENPLOT [33]. The details of calculation of the stability constants of 1 : 1 [ML] metal ion complexes by the conductometric method are described in reference [34].

3. Results and discussion

The changes in molar conductance (Λ_{m}) *versus* kryptofix5 to the silver(I) molar ratio, ($[\mathrm{L}]_{\mathrm{t}}/[\mathrm{M}]_{\mathrm{t}}$), were measured in pure AN, MeOH, H_2O, and DMSO, and also in AN-EtOAc, MeOH-EtOAc, MeOH-H_2O, and DMSO-EtOAc binary mixed solvents at

15°C, 25°C, 35°C, and 45°C. $[L]_t$ is the total concentration of the ligand and $[M]_t$ is the total concentration of the metal cation.

The molar conductance values *versus* ligand/metal cation mole ratios in MeOH–EtOAc (mol%MeOH = 25) and DMSO–EtOAc (mol%DMSO = 25) binary solutions are shown in figures 1 and 2, respectively. Addition of kryptofix5 to Ag^+ solution in the binary solvent systems at different temperatures results in an increase in molar conductivity, which indicates that the $(kryptofix5.Ag)^+$ complex is more mobile than

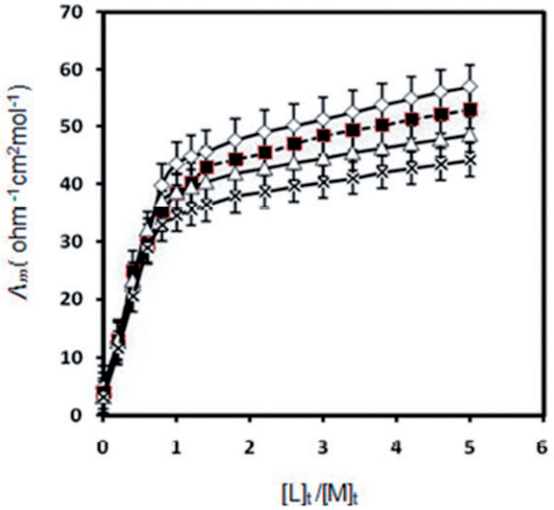

Figure 1. Molar conductance–mole ratio plots for $(kryptofix5.Ag)^+$ in MeOH–EtOAc binary solution (mol%MeOH = 25) at different temperatures (◇ 15°C, ■ 25°C, Δ 35°C, × 45°C).

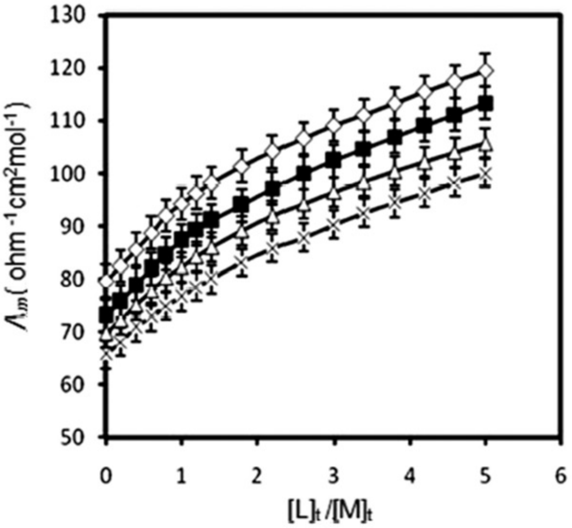

Figure 2. Molar conductance–mole ratio plots for $(kryptofix5.Ag)^+$ in DMSO–EtOAc binary solution (mol%DMSO = 25) at different temperatures (◇ 25°C, ■ 35°C, Δ 45°C, × 55°C).

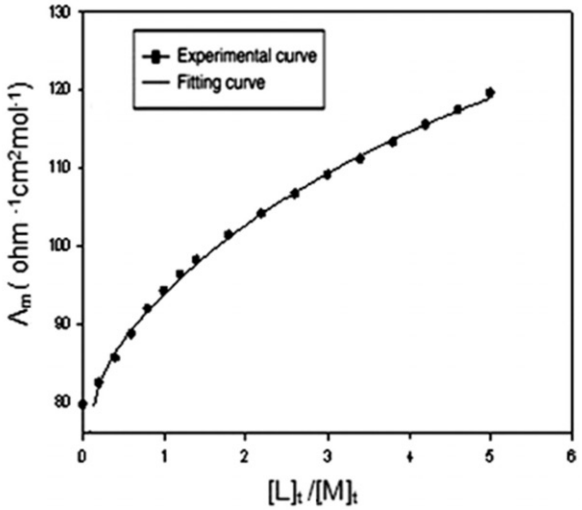

Figure 3. The fitting and experimental curves for (kryptofix5.Ag)$^+$ in DMSO–EtOAc binary solution (mol%DMSO = 25) at 25°C.

the free solvated Ag$^+$. As is evident in figure 1, the slopes of the molar conductivity curves change sharply at the point where the ligand/Ag$^+$ molar ratio is about 1, which indicates that a fairly stable 1 : 1 [ML] complex is formed in MeOH/EtOAc binary solution. As shown in figure 2, the molar conductivity curves do not show much change in their slope at the molar ratio of about 1, which emphasizes the formation of a weaker complex in DMSO–EtOAc binary solution. In order to underline the validity of the 1 : 1 [ML] complexation model, the fitting and experimental curves for (kryptofix5.Ag)$^+$ in DMSO–EtOAc binary solution (mol%DMSO = 25) at 25°C are shown in figure 3. There is very good agreement between the fitting and experimental data. Hence our assumption of 1 : 1 stoichiometry seems reasonable.

Changes in molar conductivity *versus* kryptofix5/Ag$^+$ molar ratio in pure methanol and pure AN are shown in figures 4 and 5, respectively. Interesting behavior was observed for complexation of Ag$^+$ with kryptofix5 in pure methanol. It is clear from figure 4 that addition of the ligand to the Ag$^+$ solution causes the molar conductivity to increase gradually until the mole ratio reaches 1 at 15 and 25°C and then increases sharply. It seems that addition of kryptofix5 to the Ag$^+$ in pure MeOH results in formation of a stable 1 : 1 [ML] complex at these temperatures, which is somewhat more mobile than the free Ag$^+$ solvated cation. Further addition of the ligand to the solution probably results in formation of a 1 : 2 [ML$_2$] complex which is much less solvated than the [ML] complex; therefore, the molar conductivity of the solution increases sharply beyond the kryptofix5/Ag$^+$ molar ratio of 1.

Different behavior is observed at 35°C and 45°C in pure CH_3OH. Molar conductivity decreases slowly until the mole ratio reaches 1, but further addition of the ligand to the solution results in an increase in molar conductivity. Addition of the ligand to Ag$^+$ solution at these two higher temperatures results in formation of a [ML] complex which is less mobile than free solvated Ag$^+$, but further addition of the ligand results in formation of a [ML$_2$] complex which is less solvated than the [ML] complex and,

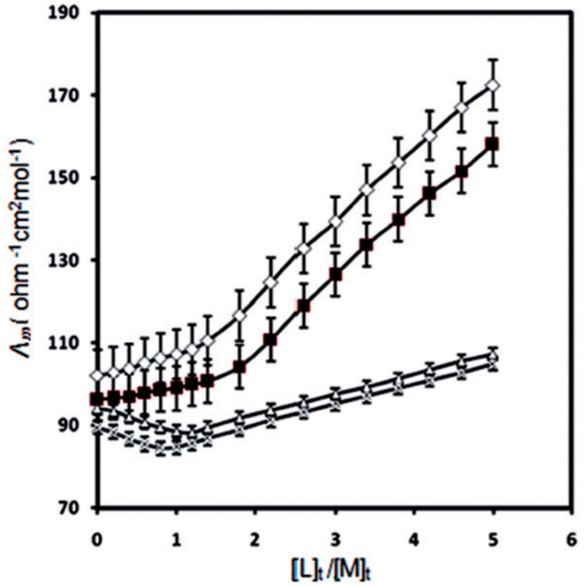

Figure 4. Molar conductance–mole ratio plots for (kryptofix5.Ag)$^+$ in pure methanol at different temperatures (♢ 15°C, ■ 25°C, Δ 35°C, × 45°C).

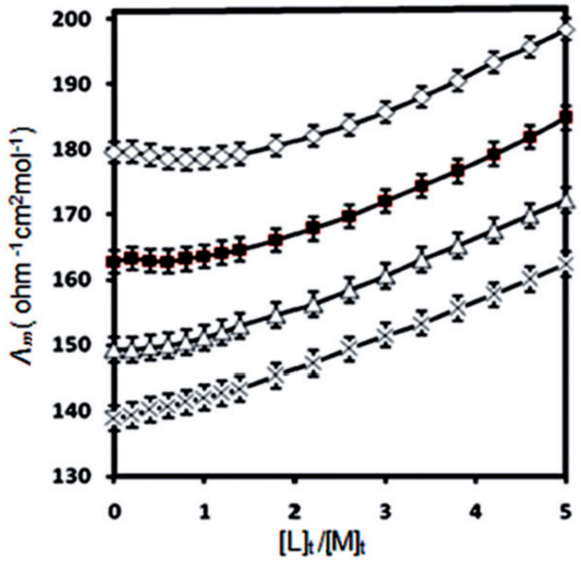

Figure 5. Molar conductance–mole ratio plots for (kryptofix5.Ag)$^+$ in pure acetonitrile at different temperatures (♢ 15°C, ■ 25°C, Δ 35°C, × 45°C).

therefore, the molar conductivity increases. Such behavior may be described according to the following equilibria:

$$Ag^+ + \text{kryptofix5} \leftrightarrow (\text{kryptofix5.Ag})^+, \tag{I}$$

$$(\text{kryptofix5.Ag})^+ + \text{kryptofix5} \leftrightarrow \left[(\text{kryptofix5})_2\text{Ag}\right]^+. \tag{II}$$

The different behavior observed in the molar conductivity curves for complexation of Ag^+ by kryptofix5 in MeOH at different temperatures may be due to changes in the solvation of the resulting complexes with temperature. Similar behavior was observed for complexation of Ag^+ with kryptofix5 in MeOH–H_2O (in all compositions) and AN–EtOAc (mol%AN = 75) binary mixed solvent solutions and in pure AN (at 25°C). The data cannot be used for calculation of the stability constant of the (kryptofix5.Ag)$^+$ complex.

As is clear from figure 5, addition of kryptofix5 to Ag^+ solution in pure AN causes the molar conductivity to increase or decrease slightly depending on the temperature until the mole ratio is 1 and then increases sharply. The behavior observed in this solvent system may be due to changes in the solvation number of Ag^+ and the resulting complexes with temperature. The results obtained in this study reveal that the mechanism of complexation between podand ligands and the metal cations may be changed by the nature and composition of the solvent system.

The stability constant of the (kryptofix5.Ag)$^+$ complex at each temperature was calculated from changes in molar conductance as a function of ligand/metal cation mole ratio using a GENPLOT computer program [33]. The values of the stability constant ($\log K_f$) for the (kryptofix5.Ag)$^+$ complex in various solvent systems are listed in table 1. Comparison of the data at 25°C reveals that the stability constant of the (kryptofix5.Ag)$^+$ complex in the binary mixed solvents decreases in the order MeOH–EtOAc > AN–EtOAc > DMSO–EtOAc. A relatively weak (kryptofix5.Ag)$^+$ complex is formed in pure DMSO and EtOAc–DMSO binary solutions. Solvating ability of a solvent, as expressed by the Gutmann donor number [35], plays an important role in complexation reactions [33, 36, 37]. There is an inverse relationship between the stabilities of the metal ion complexes and the donor ability of the solvents. DMSO with a high donor ability (DN = 29.8) relative to MeOH (DN = 20) and AN (DN = 14.1), which acts as a strong electron-pair donor and hydrogen-bond acceptor [31], can solvate Ag^+ strongly and compete with the ligand for this metal cation. The higher dielectric constant of DMSO ($\varepsilon = 45$) rather than AN ($\varepsilon = 38$) and MeOH ($\varepsilon = 32.6$) could also decrease the electrostatic interactions between the metal cation and the podand ligand.

The changes in stability constant of (kryptofix5.Ag)$^+$ *versus* the solvent composition of the EtOAc–DMSO binary mixed system at different temperatures is shown in figure 6. Changes in the stability constant ($\log K_f$) of (kryptofix5.Ag)$^+$ *versus* the composition of the binary mixed solvent certainly are not monotonic. Somewhat similar behavior was observed for other binary mixed solvent solutions. This non-linear relationship may be due to the solvent–solvent interactions between the two constituent solvent molecules which result in changing the structure of the solvent systems with their composition and, therefore, changing the solvation numbers of the cation, ligand and even the (kryptofix5.Ag)$^+$ complex in solution. Viscosity measurements for MeOH–H_2O binary mixtures have shown that the change in viscosity *versus*

Table 1. log K_f values for the (kryptofix5.Ag)$^+$ complex in AN–EtOAc, MeOH–H_2O, MeOH–EtOAc, and DMSO–EtOAc binary mixtures at different temperatures.

	log $K_f \pm$ SD[a]			
Medium	15°C	25°C	35°C	45°C
AN–EtOAc				
Pure AN	[d]	[d]	[d]	[d]
75% AN–25% EtOAc[b]	[d]	[d]	[d]	[d]
50% AN–50% EtOAc	3.61 ± 0.05	3.83 ± 0.05	3.83 ± 0.04	3.87 ± 0.06
25% AN–75% EtOAc	4.53 ± 0.06	3.90 ± 0.02	3.82 ± 0.02	4.45 ± 0.07
10% AN–90% EtOAc	4.84 ± 0.11	4.71 ± 0.09	4.63 ± 0.09	4.48 ± 0.08
Pure EtOAc	[c]	[c]	[c]	[c]
MeOH–H_2O				
Pure MeOH	[d]	[d]	[d]	[d]
75% MeOH–25% H_2O[b]	[d]	[d]	[d]	[d]
50% MeOH–50% H_2O	[d]	[d]	[d]	[d]
25% MeOH–75% H_2O	[d]	[d]	[d]	[d]
Pure H_2O	2.70 ± 0.11	2.83 ± 0.07	2.68 ± 0.08	2.75 ± 0.21
MeOH–EtOAc				
Pure MeOH	[d]	[d]	[d]	[d]
75% MeOH–25% EtOAc[b]	[d]	[d]	2.59 ± 0.02	2.73 ± 0.14
50% MeOH–50% EtOAc	3.87±0.10	3.95±0.09	4.04±0.09	4.12±0.10
25% MeOH–75% EtOAc	3.87 ± 0.10	3.95 ± 0.09	4.04 ± 0.09	4.12 ± 0.10
Pure EtOAc	[c]	[c]	[c]	[c]
DMSO–EtOAc	25°C	35°C	45°C	55°C
Pure DMSO	2.74 ± 0.11	2.55 ± 0.14	2.56 ± 0.13	2.56 ± 0.12
75% DMSO–25% EtOAc[b]	2.56 ± 0.13	2.56 ± 0.13	2.49 ± 0.23	2.68 ± 0.07
50% DMSO–50% EtOAc	2.83 ± 0.09	2.63 ± 0.09	2.54 ± 0.17	2.60 ± 0.07
25% DMSO–75% EtOAc	3.53 ± 0.05	3.45 ± 0.04	3.49 ± 0.03	3.31 ± 0.03
10% DMSO–90% EtOAc	4.41 ± 0.07	4.31 ± 0.06	4.26 ± 0.05	4.16 ± 0.04
Pure EtOAc	[c]	[c]	[c]	[c]

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

composition of this mixed solvent passes through a maximum which indicates a strong interaction between water and methanol molecules [38]. In addition, the hetero-selective solvation of the cation and the ligand and the character of its changes with composition of the mixed solvents may effect the complexation reaction between Ag^+ and kryptofix5 in these mixed solvent solutions.

The thermodynamic equilibrium constant, K_f, is related to the Gibbs standard free energy of the complexation reaction (ΔG^0_c). The changes in the standard enthalpy (ΔH^0_c) for the complexation reaction were obtained from the slope of the van't Hoff plots assuming that C_P is equal to zero over the entire temperature range investigated and the changes in standard entropy (ΔS^0_c) were calculated from the relationship $\Delta G^0_{c,298.15} = \Delta H^0_c - 298.15 \Delta S^0_c$. The values of the standard thermodynamic parameters, summarized in table 2, show that in most cases the complex is both enthalpy and entropy stabilized. As evident from table 1, in the case of some pure and mixed solvents, the stability constant of the resultant complex does not change significantly with temperature, hence, the values of ΔH^0_c were considered nearly 0 in table 2. It seems that

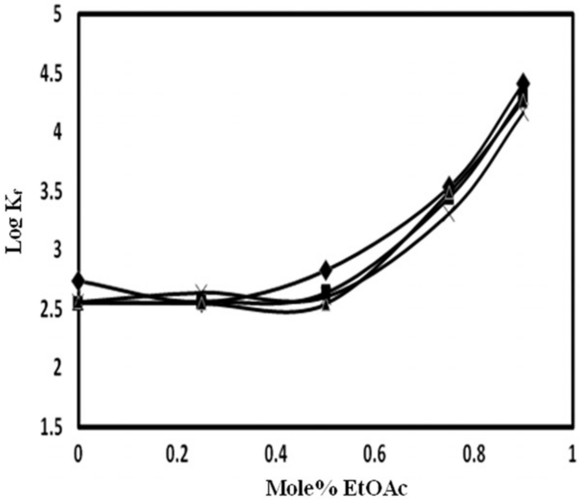

Figure 6. Changes of stability constant (log K_f) of (kryptofix5.Ag)$^+$ with composition of the EtOAc–DMSO binary system at different temperatures (◇15°C, ■ 25°C, ▲35°C, × 45°C).

Table 2. Thermodynamic parameters for formation of the (kryptofix5.Ag)$^+$ complex in AN–EtOAc, MeOH–EtOAc, and DMSO– EtOAc binary mixtures and in pure H_2O.

Medium	$\Delta S^0_C + SD^a$ ($J\,mol^{-1}\,K^{-1}$)	$\Delta H^0_C + SD^a$ ($kJ\,mol^{-1}$)	$\Delta G^0_C + SD^a$ (25°C) ($kJ\,mol^{-1}$)	log $K_f \pm SD^a$ (25°C)
AN–EtOAc				
50% AN–50% EtOAc^b	3.83 ± 0.05	-21.9 ± 0.3	13.7 ± 5.8	119 ± 19
25% AN–75% EtOAc	3.90 ± 0.02	-22.3 ± 0.9	44.2 ± 16.1	223 ± 54
10% AN–90% EtOAc	4.71 ± 0.09	-26.9 ± 0.5	-20.4 ± 1.5	22 ± 5
MeOH–EtOAc				
50% MeOH–50% EtOAc^b	3.95 ± 0.09	-22.5 ± 0.5	14.4 ± 0.4	124 ± 1
25% MeOH–75% EtOAc	4.83 ± 0.11	-27.5 ± 0.6	~0	156 ± 46
DMSO–EtOAc				
Pure DMSO^b	2.74 ± 0.11	-15.6 ± 0.6	~0	^{c}
75% DMSO–25% EtOAc^b	2.56 ± 0.13	-14.6 ± 0.7	~0	66 ± 23
50% DMSO–50% EtOAc	2.83 ± 0.09	-16.1 ± 0.5	~0	^{c}
25% DMSO–75% EtOAc	3.53 ± 0.05	-20.1 ± 0.3	-11.2 ± 5.5	^{c}
10% DMSO–90% EtOAc	4.41 ± 0.07	25.2 ± 0.4	-15.0 ± 1.4	34 ± 5
Pure H_2O	2.83 ± 0.07	-16.2 ± 0.4	~0	54 ± 22

[a] SD = Standard deviation.
[b] Composition of binary mixtures is expressed in mol% for each solvent system.
[c] With high uncertainty.

the complexation process between kryptofix5 and Ag$^+$ is athermic in those solvent systems.

The summarized thermodynamic data in table 2 show that the standard thermodynamic quantities (ΔH^0_c and ΔS^0_c) for complexation between kryptofix5 and Ag$^+$ do not vary monotonically with solvent composition. The reaction entropy for the complexation process is due to variations in the contribution of important parameters such as changes in the flexibility and conformational changes of the acyclic ligand during the

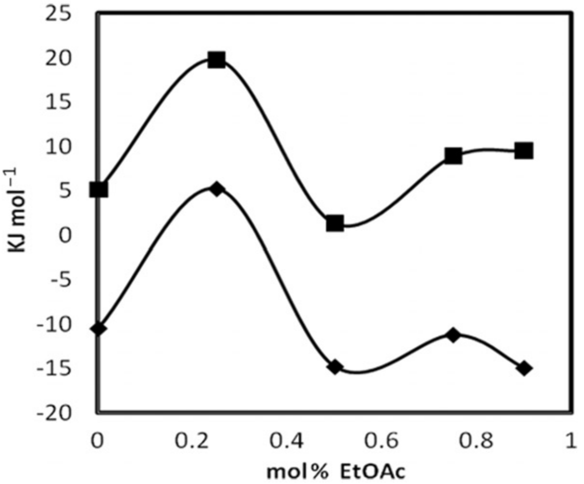

Figure 7. Changes of ΔH_c^0 (■) and $T\Delta S_c^0$ (◇) for formation of $(\text{kryptofix5.Ag})^+$ at 25°C.

complexation process, and also with the extent of cation–solvent, ligand–solvent, and complex–solvent interactions and even with the solvent–solvent interactions [39]. The changes of the enthalpy of the ligand by complexation are mainly due to changes in solvation, intramolecular ligand–ligand repulsion, the stacking of the aromatic residues, and steric deformation of the ligand induced by the bound metal ion [40]. The changes in the standard thermodynamic parameters for complexation of Ag^+ by kryptofix5 with the mole fraction of EtOAc in EtOAc–DMSO binary mixed solvent solutions are shown in figure 7. Changes in ΔH_c^0 and $T\Delta S_c^0$ with solvent composition of this solvent system are not linear. This behavior may reflect changes occurring in the structural distribution of solvent in the solvent mixtures which may result in the preferential solvation of Ag^+ and the acyclic ligand by DMSO molecules.

4. Conclusion

The results obtained in this study show that in most binary mixed solvent solutions the acyclic crown ether (kryptofix5) forms a 1 : 1 [ML] complex with silver(I), but in the case of pure MeOH and pure AN, and also in some of the binary mixed solvent solutions, in addition to formation of a 1 : 1 [ML] complex, a 1 : 2 $[ML_2]$ complex forms in solution. The conductance data show that the solvation numbers of Ag^+ and the resulting complexes change with temperature. The order of the stability constant ($\log K_f$) for the $(\text{kryptofix5.Ag})^+$ complex in the binary mixed solvent solutions at 25°C was MeOH–EtOAc > AN–EtOAc > DMSO–EtOAc. The results show that the electron donor ability of the solvent plays an important role in complexation. A non-monotonical behavior was observed for changes of the stability constant ($\log K_f$) of $(\text{kryptofix5.Ag})^+$ *versus* the composition of the mixed solvents. The deviations from the linear behavior can be due to the extent of preferential solvation and the existence of specific solvent–solvent and solvent–solute interactions. The changes in thermodynamic parameters with solvent composition were not linear. This behavior may be due to changes in the structure of the binary solvents as the composition of the medium is varied. In most cases, the $(kryptofix5.Ag)^+$ complex is both enthalpy and entropy stabilized.

Based on the conductometric data obtained for complexation of kryptofix5 with Ag^+ in acetonitrile, ethyl acetate, methanol, water, and dimethyl sulfoxide, and some of their binary mixtures at different temperatures, we can conclude that the stoichiometry, stability, and also the thermodynamics of complexation between the podand ligand and Ag^+ may be governed by the nature and composition of the solvent system and also by changing the temperature.

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