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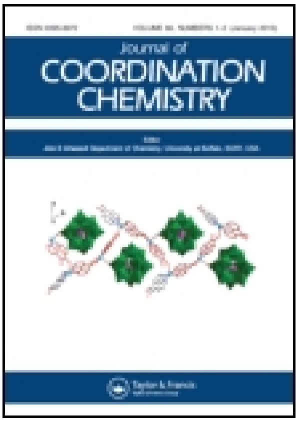

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Solvent influence upon complex formation between kryptofix5 and Cd^{2+} in some pure and binary mixed non-aqueous solvents using conductometry

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The complexation reaction of Cd^{2+} with 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (kryptofix5) was studied in pure acetonitrile (AN), ethylacetate (EtOAc), methanol (MeOH), dimethylformamide (DMF), and in acetonitrile-ethylacetate (AN–EtOAc), acetonitrile-dimethylformamide (AN–DMF), methanol-acetonitrile (MeOH–AN), and dimethylformamide-ethylacetate (DMF–EtOAc) binary mixed solvent solutions at different temperatures using conductometric method. The conductance data show that the stoichiometry of the complex in all solvent systems, is 1 : 1 [ML]. The fitting and experimental curves were obtained from Sigma plot computer program to make it more clear of the 1 : 1 [ML] complexation model. The stability constant of $(\text{kryptofix5}\cdot\text{Cd})^{2+}$ complex was obtained using a GENPLOT computer program. The results show that the stability of $(\text{kryptofix5}\cdot\text{Cd})^{2+}$ complex at all studied temperatures in the binary solvent solutions decreases in order: AN–EtOAc > AN–MeOH > AN–DMF ~ EtOAc–DMF and in pure non-aqueous solvents, the stability order of the complex was found to be: AN > EtOAc > MeOH > DMF. The values of standard thermodynamic parameters (ΔH°_c, ΔS°_c) for formation of the complex were obtained from temperature dependence of the stability constant using the van't Hoff plot. The results show that in most cases, the complex formation reaction between kryptofix5 and Cd^{2+} is entropy stabilized.

Keywords: Cd^{2+}; 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (kryptofix5); Mixed nonaqueous solutions; Conductometry

1. Introduction

The early work of Pederson, has led to synthesis of an enormous variety of functionalized crown, and crown analogues with varying selectivity for an enormous variety of guest species. Podands are the most important polyethers among those crown analogues which is coined by Vögtle and Weber [1]. These acyclic crown ethers have a linear part that can form a wrap around the metal cations in a very similar way to that of the cyclic species [2,3]. The interactions between these ligands and metal cations are generally noncovalent in nature [4]. The stability of the complexes resulting from kryptofix5 arises from two factors: the ethereal oxygens and the aromatic residues which control the strength of complexation by π-electron interactions, steric influences, and by supplying two nitrogen atoms

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[1,5,6]. In recent years, polypodands represent a valid alternative to the cyclic analogues of crown ethers and cryptands because of their substantially lower cost, relative nontoxicity, and high effectiveness in homogeneous and heterogeneous systems [7]. 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane with trade name of kryptofix5, is an open chain polyether bearing quinoline end groups, which can be considered as a key podand due to its attractive characteristics. It has an intermediate affinity for alkali metal ions and neutral molecules in solution and solid states [1]. There are some reports on the thermodynamics of complexation of podands with some alkaline metals [8,9], alkaline earth metals [10] and transition, and heavy metal ions [11,12] in some pure non-aqueous solvents.

Podands generally have a high degree of flexibility on binding a guest and the conformational change that produces a stable host–guest complex [13]. There have been several applications of podands, in construction of chemically modified electrodes [14] and phase transfer catalysis [7]. Also they have been used for potentiometric detection of organic acids [15]. These applications have generated a great deal of interest in podand metal-ion complexes.

Cadmium is not mined, but it is a byproduct obtained on the smelting of other metals such as zinc, lead, and copper. Cadmium is used as a component in cadmium pigments, coatings, and is commonly used in electroplating. Cadmium interferes in the metabolism of human body fats by replacing zinc in this process. It can be released from car exhaust, metal processing industries, battery and paint manufacturing, and waste hauling and disposal activities. Humans absorb cadmium from food and the environment. Cadmium ions may replace calcium ions in bones preventing proper bone repair. It is, therefore, necessary to use the analytical methods for monitoring and control of cadmium in environment.

It is known that the solvent effects play an important role in stability constant of formed complexes in solutions. The widespread use of non-aqueous solvents has contributed greatly to later advances in chemical sciences and technologies [16,17]. Owing to the changing of solvation capacities of the ligands and the metal cations with changing the mixed solvent compositions, the recent studies on complex formation of polyethers with metal cations have been carried out in some mixed solvent solutions [18,19]. Nevertheless, there has been a very limited extent of studies on complex formation of podands in such media.

Various techniques, such as potentiometry [20], calorimetry [21], conductometry [22], NMR spectrometry [23], spectrophotometry [24], and polarography [25,26] have been used to study the complexation of a range of ligands with different metal cations in a variety of non-aqueous and mixed solvent solutions. In recent years, we have employed the conductance measurements as a sensitive and inexpensive method for such investigations [27–29]. By conductometry, we are able to investigate the effect of solvent on stability constant of complex formation in pure and mixed solvent solutions and their effect on thermodynamic parameters such as enthalpy, entropy, and free energy of complexation processes in solutions. Conductometry also gives information about the stoichiometry of complexation of various ligands with metal cations. The advantage of conductometry is that the measurements can be carried out with high precision at very low concentrations in solution systems.

In order to investigate the effect of the nature and composition of the solvent system upon complexation reaction of kryptofix5 with Cd^{2+}, we studied the complexation process between this acyclic crown ether and the metal cation by conductometric method. Here, we report the results obtained for the stoichiometry, stability, and also the thermodynamic parameters for formation of $(\text{kryptofix5}\cdot\text{Cd})^{2+}$ complex in acetonitrile (AN), ethylacetate (EtOAc), methanol (MeOH) and dimethylformamide (DMF) and in their binary mixtures at different temperatures.

2. Experimental

2.1. *Reagents and apparatus*

1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (kryptofix5, figure 1) and cadmium nitrate 4-hydrate were purchased from Merck (>99% purity) and were used without further purification. The solvents: EtOAc, MeOH, AN, and DMF all from Merck company were used with the highest purity.

The conductance measurements were performed on a digital Jenway conductivity apparatus, model 4510, at a frequency of 1 kHz with the use of a specially designed water jacketed cell (150 mL, Pyrex) equipped with a magnetic stirrer and was connected to a thermostated circulator water bath. The temperature of the reaction was controlled using a thermostated circular water bath (LAUDA) with a precision of ±0.1 °C equipped with a refrigerating unit.

2.2. *Procedure*

The experimental procedure to obtain the stability constant of $(\text{kryptofix5}\cdot\text{Cd})^{2+}$ complex is as follows: a solution of metal salt (1.0×10^{-4} M) was placed in a titration cell and the conductance of the solution was measured, then a step by step increase of the ligand solution prepared in the same solvent (2.0×10^{-3} M) was carried out using a precalibrated micropipette. In both of the dilute solutions, in order to keep the electrolyte concentration constant during the titration, both the starting solution and the titrant had the same metal-ion concentration.

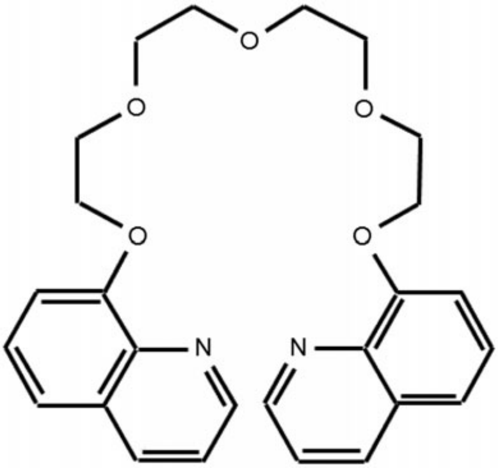

Figure 1. Structure of 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (kryptofix5).

3. Results and discussion

The changes of molar conductance (Λ_m) vs. the ligand (kryptofix5) to the cadmium (II) cation molar ratio, ($[L]_t/[M]_t$), for complexation of kryptofix5 with Cd^{2+}, in pure AN, EtOAc, MeOH, and DMF, and also in AN–EtOAc, AN–MeOH, AN–DMF, and EtOAc–DMF binary mixed solvent solutions were studied at different temperatures (15 °C, 25 °C, 35 °C, and 45 °C). $[L]_t$ is the total concentration of the kryptofix5 and $[M]_t$ is the total concentration of the metal cation (Cd^{2+}). Two typical series of molar conductance values as a function of $[L]_t/[M]_t$ in AN–EtOAc (mol% AN = 75) and AN–DMF (mol% AN = 75) binary solvent solutions are shown in figures 2 and 4, respectively. As it is obvious from these figures, addition of the ligand to the Cd^{2+} ion solution, results in an increase of molar conductivity which indicates that the $(\text{kryptofix5}\cdot Cd)^{2+}$ complex is more mobile than free solvated Cd^{2+} ion. Since, $(\text{kryptofix5}\cdot Cd)^{2+}$ complex is less solvated compared to cadmium (II) cation in solution, therefore, the mobility of the complex is higher than free solvated Cd^{2+}. As it is evident from figure 2, the slope of the corresponding molar conductivity vs. $[L]_t/[M]_t$ plot changes at the point where the ligand to cation mole ratio is about one, which is an evidence for formation of a 1 : 1 [ML] complex between kryptofix5 and Cd^{2+} in this solvent system. A similar behavior was observed in most of the studied solvents. In order to make more clear, the 1 : 1 [ML] complexation model, the fitting and experimental curves for the $(\text{kryptofix5}\cdot Cd)^{2+}$ complex in AN–EtOAc binary mixture (mol % AN = 75) at 25 °C are shown in figure 3. As is clear from this figure, there is a good agreement between the fitting and experimental data and hence, our assumption of 1 : 1 stoichiometry seems reasonable. As is evident from figure 4, the slope of the molar conductivity vs. molar ratio curves at different temperatures increases slightly in AN–DMF

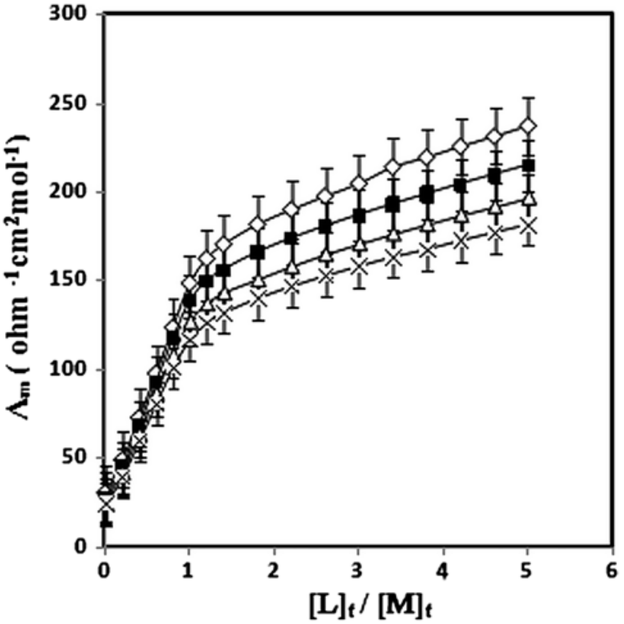

Figure 2. Molar conductance-mole ratio plots for $(\text{kryptofix5}\cdot Cd)^{2+}$ complex in AN–EtOAc binary solution (mol % AN = 75) at different temperatures (◊, 15 °C; ■, 25 °C; Δ, 35 °C; ×, 45 °C).

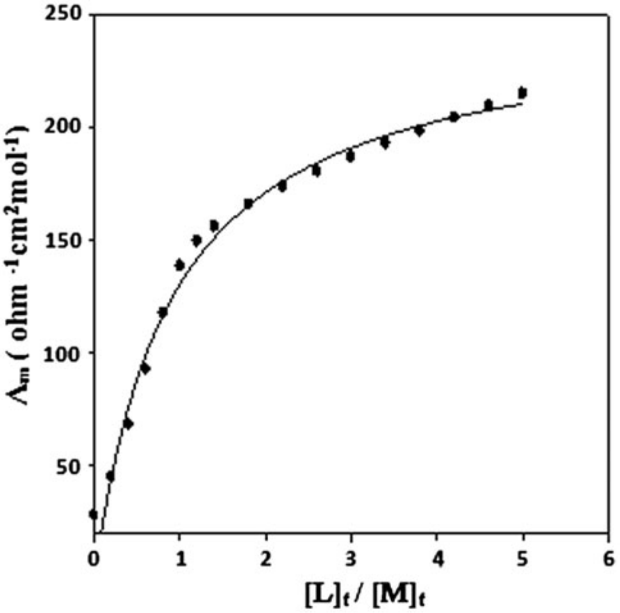

Figure 3. The fitting and experimental curves for (kryptofix5·Cd)$^{2+}$ complex in AN–EtOAc binary solution (mol % AN = 75) at 25 °C.

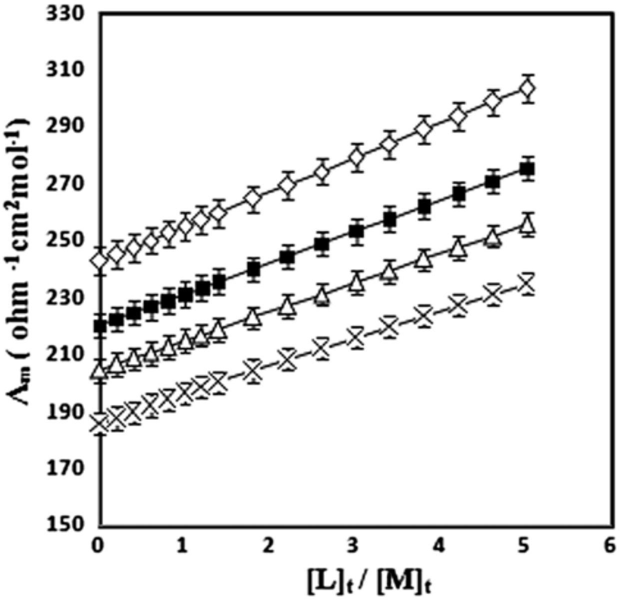

Figure 4. Molar conductance-mole ratio plots for (kryptofix5·Cd)$^{2+}$ complex in AN–DMF binary solution (mol % AN = 75) at different temperatures (◊, 15 °C; ■, 25 °C; Δ, 35 °C; ×, 45 °C).

binary mixed solvent, emphasizing the lower stability of the resulting complex in this binary solvent solution compared to the other solvent systems.

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

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

The corresponding equilibrium constant, K_f, is given by:

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} \times \frac{f_{ML^{n+}}}{f_{M^{n+}} f_L} \tag{2}$$

where $[ML^{n+}]$, $[M^{n+}]$, [L], and f, represent the equilibrium molar concentrations of the complex, free cation, free ligand and the activity coefficient of the species indicated, respectively [30]. In this article, L = kryptofix5 and $M^{n+} = Cd^{2+}$. Under the very dilute conditions, where the ionic strength is less than 0.001 M, which we employed in these experiments, the activity coefficient of the uncharged ligand, f_L, can be assumed to be unity [31]. In addition, using the Debye–Huckel limiting law for electrolytes [32], leads to the calculation that ${f_{ML}}^{n+} \approx {f_M}^{n+}$, thus, the equilibrium constant obtained in this study is the thermodynamic equilibrium constant.

The mass balance equation of 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].

$$C_M = [M^{n+}] + [ML^{n+}] \tag{3}$$

$$C_L = [L] + [ML^{n+}] \tag{4}$$

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

$$K_f[L]^2 + (1 + K_f(C_M - C_L))[L] - C_L = 0 \tag{5}$$

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

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

where,

$$[L] = C_L - \frac{C_M(\Lambda_M - \Lambda_{obs})}{\Lambda_M - \Lambda_{ML}} \tag{7}$$

Here, Λ_M is the molar conductance of the metal nitrate before addition of the ligand, Λ_{obs} the molar conductance of 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 nonlinear least squares program, GENPLOT [33].

The values of the stability constant (log K_f) for the (kryptofix5·Cd)$^{2+}$ complex in various solvent systems are listed in table 1. Comparison of the data given in this table reveals that, the order of stability constant of (kryptofix5·Cd)$^{2+}$ complex in pure studied solvents is: AN > EtOAc > MeOH > DMF, which is consistent with the order of solvation ability as expressed by Gutmann donor number of these organic solvents. In a solvent with a high solvation ability (high donor number), such as DMF (DN = 26.6), the resultant complex tends to be weak, since this solvent solvates the cation strongly and competes with the ligand for the Cd^{2+} cation, but in the solvents with lower donicity such as acetonitrile (DN = 14.1), ethylacetate (DN = 17.1), and methanol (DN = 20.0), the complex is more stable compared to DMF.

The stability of (kryptofix5·Cd)$^{2+}$ complex in the binary mixed solvent solutions decreases in the order: AN–EtOAc > AN–MeOH > AN–DMF ~ EtOAc–DMF which can be referred to solvating ability of the pure solvents which form the mixtures. Therefore, due to the lower donor ability of EtOAc relative to MeOH and DMF, a more stable complex is formed in AN–EtOAc compared with AN–MeOH and AN–DMF binary solvent solutions.

As is seen in figure 5, the changes of the stability constant (log K_f) of (kryptofix5·Cd)$^{2+}$ complex vs. the composition of AN–MeOH binary system at various temperatures are not linear. Somewhat similar behavior was observed in the case of the other binary solvent solutions. This behavior is probably due to the some kinds of solvent–solvent interactions which results in changing the solvation properties of the acyclic polyether, cation, and even the

Table 1. Log K_f values of (kryptofix5·Cd)$^{2+}$ complex in AN–EtOAc, AN–MeOH, AN–DMF and EtOAc–DMF binary mixtures at different temperatures.

	Log K_f ± SD[a]			
Medium	15 °C	25 °C	35 °C	45 °C
AN–MeOH				
Pure AN	4.3 ± 0.1	4.3 ± 0.1	4.3 ± 0.1	4.30 ± 0.09
75% AN–25% MeOH[b]	3.9 ± 0.1	4.00 ± 0.9	4.1 ± 0.1	4.15 ± 0.08
50% AN–50% MeOH	3.13 ± 0.07	3.32 ± 0.06	3.49 ± 0.07	3.42 ± 0.06
25% AN–75% MeOH	2.8 ± 0.1	2.8 ± 0.1	2.8 ± 0.1	3.0 ± 0.1
Pure MeOH	2.7 ± 0.1	2.7 ± 0.1	2.78 ± 0.09	2.81 ± 0.07
AN–EtOAc				
Pure AN	4.28 ± 0.1	4.3 ± 0.1	4.3 ± 0.1	4.30 ± 0.09
75% AN–25% EtOAc[b]	4.31 ± 0.07	4.38 ± 0.07	4.37 ± 0.07	4.38 ± 0.07
50% AN–50% EtOAc	4.73 ± 0.09	4.70 ± 0.09	4.72 ± 0.09	4.7 ± 0.1
25% AN–75% EtOAc	4.14 ± 0.09	4.2 ± 0.1	4.2 ± 0.2	4.3 ± 0.3
Pure EtOAc	3.85 ± 0.05	3.70 ± 0.06	3.70 ± 0.06	3.30 ± 0.04
AN–DMF				
Pure AN	4.3 ± 0.1	4.3 ± 0.1	4.3 ± 0.1	4.30 ± 0.09
75% AN–25% DMF[b]	2.6 ± 0.1	2.7 ± 0.1	2.7 ± 0.1	2.77 ± 0.09
50% AN–50% DMF	2.7 ± 0.1	2.7 ± 0.1	2.7 ± 0.1	2.78 ± 0.09
25% AN– 75% DMF	2.5 ± 0.2	2.7 ± 0.1	2.5 ± 0.1	2.79 ± 0.08
Pure DMF	2.7 ± 0.1	2.7 ± 0.1	2.5 ± 0.1	2.61 ± 0.08
EtOAc–DMF				
Pure EtOAc	3.85 ± 0.05	3.70 ± 0.06	3.70 ± 0.06	3.30 ± 0.04
75% EtOAc–25% DMF[b]	2.60 ± 0.09	2.6 ± 0.1	2.64 ± 0.06	2.67 ± 0.07
50% EtOAc–50% DMF	2.5 ± 0.2	2.63 ± 0.06	2.5 ± 0.1	2.61 ± 0.07
25% EtOAc–75% DMF	2.5 ± 0.2	2.6 ± 0.1	2.6 ± 0.1	2.61 ± 0.07
Pure DMF	2.7 ± 0.1	2.7 ± 0.1	2.5 ± 0.1	2.61 ± 0.08

[a] SD = Standard deviation.

[b] Composition of binary solvents is expressed in mol % for each solvent system.

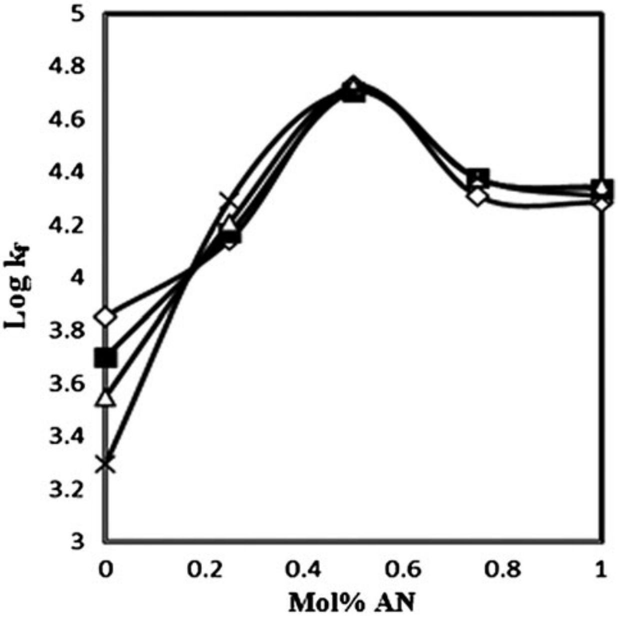

Figure 5. Changes of stability constant (log K_f) of (kryptofix5·Cd)$^{2+}$ complex with the composition of the AN–EtOAc binary system at different temperatures: (◊, 15 °C; ■, 25 °C; △, 35 °C; ×, 45 °C).

resultant complex in these solvent mixtures. The interactions between some binary mixed solvents have been investigated. As an example, it has been shown that mixing of DMF with

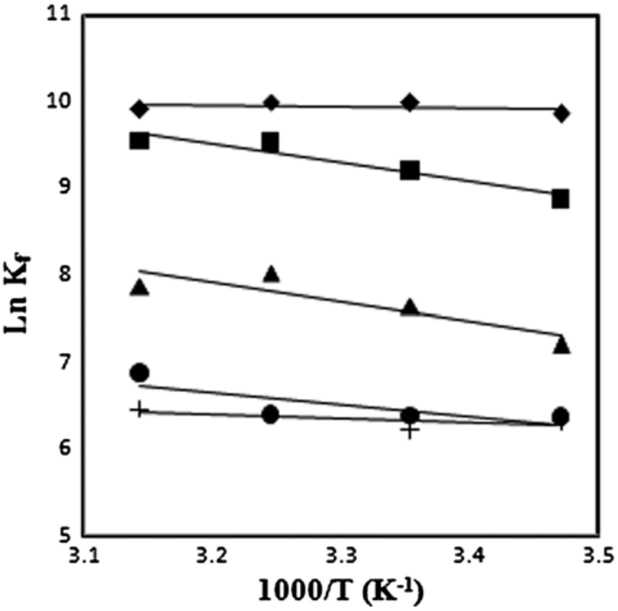

Figure 6. van’t Hoff plots for (kryptofix5·Cd)$^{2+}$ complex in AN–MeOH binary systems: (mol % AN: ♦, 100; ■, 75; ▲, 50; ●, 25; +, 0).

AN induces the mutual destruction of dipolar structures of these dipolar aprotic liquids and releasing the free dipoles [34]. Hence, strong dipolar interactions between AN and DMF molecules are expected. In addition, there is an interaction between the AN and MeOH molecules ($K_{\mathrm{ass}} = 1.23$), via hydrogen bonding in their binary mixtures [35].

The thermodynamic equilibrium constant, K_{f}, is related to Gibbs standard free energy of complexation reaction, ($\Delta G_{\mathrm{c}}^{\circ}$). The van't Hoff plots of ln K_{f} vs. $1/T$ for $(\text{kryptofix5}\cdot\text{Cd})^{2+}$ complex in AN–MeOH binary systems are shown in figure 6. Plots of ln K_{f} vs. $1/T$ in all cases were linear. The changes in the standard enthalpy ($\Delta H_{\mathrm{c}}^{\circ}$) for 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 ($\Delta S_{\mathrm{c}}^{\circ}$) were calculated from the relationship $\Delta G_{\mathrm{c},298.15}^{\circ} = \Delta H_{\mathrm{c}}^{\circ} - 298.15\ \Delta S_{\mathrm{c}}^{\circ}$. The values of standard thermodynamic parameters which are given in table 2, demonstrate that in most cases, the complex is entropy stabilized, as it is evident in table 1, in the case of some pure and binary mixed solvents, the stability constant (log K_{f}) of $(\text{kryptofix5}\cdot\text{Cd})^{2+}$ complex, has a little temperature variation, hence, the values of $\Delta H_{\mathrm{c}}^{\circ}$ were considered nearly zero in table 2. It seems that the complexation process between kryptofix5 and Cd^{2+} is athermic in these solvent systems. The thermodynamic data in table 2 also shows, that in some of the studied solvents, the complexation process is exothermic or endothermic depending on the nature and composition of the solvent system.

Table 2. Thermodynamic parameters for formation of $(\text{kryptofix5}\cdot\text{Cd})^{2+}$ complex in AN–EtOAc, AN–MeOH, AN–DMF and EtOAc–DMF binary mixtures.

Medium	$\Delta G_{\mathrm{c}}^{\circ} \pm$ SD[a] (25 °C) (kJ/mol)	$\Delta H_{\mathrm{c}}^{\circ} \pm$ SD[a] (kJ/mol)	$\Delta S_{\mathrm{c}}^{\circ} \pm$ SD[a] (J/molK)
AN–MeOH			
Pure AN	24.7 ± 0.6	~0	87 ± 8
75% AN–25% EtOAc[b]	22.8 ± 0.5	18 ± 4	137 ± 12
50% AN–50% EtOAc	19.0 ± 0.3	18 ± 7	125 ± 24
25% AN–75% EtOAc	15.8 ± 0.8	12 ± 6	93 ± 21
Pure MeOH	15.4 ± 0.7	~0	66 ± 9
AN–EtOAc			
Pure AN	24.7 ± 0.6	~0	87 ± 8
75% AN–25% EtOAc[b]	25.0 ± 0.4	~0	96 ± 7
50% AN–50% EtOAc	26.8 ± 0.5	~0	87 ± 3
25% AN–75% EtOAc	23.8 ± 0.8	8 ± 2	108 ± 5
Pure EtOAc	21.1 ± 0.3	−32 ± 4	−36 ± 12
AN–DMF			
Pure AN	24.7 ± 0.6	~0	87 ± 8
75% AN–25% DMF[b]	15.4 ± 0.7	11 ± 3	90 ± 9
50% AN–50% DMF	15.4 ± 0.7	~0	66 ± 8
25% AN–75% DMF	15.7 ± 0.6	~0	87 ± 37
Pure DMF	15.6 ± 0.6	~0	c
EtOAc–DMF			
Pure EtOAc	21.1 ± 0.3	−32 ± 4	−36 ± 12
75% EtOAc–25% DMF[b]	14.7 ± 0.7	~0	64 ± 8
50% EtOAc–50% DMF	15.0 ± 0.3	~0	60 ± 14
25% EtOAc–75% DMF	14.8 ± 0.5	5 ± 2	65 ± 5
Pure DMF	15.6 ± 0.6	~0	c

[a] SD = Standard deviation.

[b] Composition of binary mixtures is expressed in mol% for each solvent system.

[c] With high uncertainty.

As is evident in table 2, it can be concluded that the standard thermodynamic quantities (ΔH_c° and ΔS_c°) for complexation process between kryptofix5 and Cd^{2+} do not vary monotonicaly with the solvent composition. The changes of the enthalpy of the ligand by complexation are mainly for changing the solvation, interamolecular ligand–ligand repulsion, the stacking of the aromatic residues and steric deformation of the ligand induced by the bond metal ion [36]. The reaction entropy for the complexation process changes due to the flexibility and conformation of the acyclic ligand during the complexation process, and also with the extent of cation–solvent, ligand–solvent and complex–solvent interactions and even with the solvent–solvent interactions [37]. Therefore, we should not expect a monotonic relationship between these thermodynamic quantities and the solvent composition of the binary mixed solvent solutions.

4. Conclusion

The experimental results obtained in this study, show that in all studied solvent systems, the acyclic crown ether (kryptofix5) forms a 1 : 1 [ML] complex with cadmium (II) cation. The order of stability constant ($\log K_f$) of $(\text{kryptofix5}\cdot\text{Cd})^{2+}$ complex in the binary mixed solvent at all studied temperatures was found to be: AN–EtOAc > AN–MeOH > AN–DMF ∼ EtOAc–DMF and in the pure non-aqueous solvents, the stability order of the complex decreases in order of: AN > EtOAc > MeOH > DMF. The results show that the electron donor ability of the solvent plays an important role in the complexation reaction. A non-monotonicaly behavior was observed for changes of the stability constant ($\log K_f$) of $(\text{kryptofix5}\cdot\text{Cd})^{2+}$ complex vs. the composition of the mixed solvents. The deviations from the linear behavior can be due to the extent of preferential solvation of the dissolved species and the existence of specific solvent–solvent and solvent–solute interactions. In most cases, the $(\text{kryptofix5}\cdot\text{Cd})^{2+}$ complex is both enthalpy and entropy stabilized. Based on the conductometric data which are obtained for complexation of kryptofix5 with the Cd^{2+} in AN, EtOAc, MeOH, DMF, and some of their binary mixtures at different temperatures, we can conclude that the stability and also the thermodynamics of complexation processes between the podand ligands and the metal cations may be governed by nature and composition of the solvent system.

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