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Review Article

Complex Formation of 1,10-Dibenzyl-1,10-diaza-18-crown-6 with Ni^{2+}, Cu^{2+}, Ag^{+} and Cd^{2+} Metal Cations in Acetonitrile–dimethylformamide Binary Solutions

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Key words: 1,10-Dibenzyl-1,10-diaza-18-crown-6, Ni^{2+}, Cu^{2+}, Ag^{+} and Cd^{2+} metal cations, Acetonitrile–dimethylformamide binary mixtures, Conductometry

Abstract

Conductance measurements are reported for nickel(II), cupper(II), silver(I) and cadmium(II), salts in acetonitrile (AN)–dimethylformamide (DMF) binary solvents containing macrocyclic ligand, 1,10-dibenzyl-1,10-diaza-18-crown-6 (DBDA18C6) at different temperatures. The changes in molar conductance caused by addition of DBDA18C6 to solutions were analyzed by non-linear least squares to give stability constants of 1:1 metal cation–DBDA18C6 complexes. The results show that the stabilities of the complexes are sensitive to solvent composition and in some cases the sequence of stabilities is changed with changing the composition of the mixed solvents. The values of thermodynamic quantities ($\Delta H°c$ and $\Delta S°c$) for formation of DBDA18C6-Ni^{2+}, DBDA18C6-Cu^{2+}, DBDA18C6-Ag^{+} and DBDA18C6-Cd^{2+} complexes were obtained from temperature dependence of the stability constants and the results show that the values of $\Delta H°c$ and $\Delta S°c$ for these complexes are sensitive to the nature and composition of AN–DMF binary solutions, but they do not vary monotonically with the solvent composition.

Introduction

Since the first report [1] on the synthesis of crown ethers, there has been a vast amount of research carried out with respect to characterization of the structures and stereochemical dynamics as well as to complexing ability of these compounds. Crown ethers can form host–guest complexes [2] with many metal ions, particularly with alkali and alkaline earth metal cations. An important property of crown ethers is their ability in formation of stable complexes with metal ions. In a typical complex, the metal ion occupies a site in the center of the crown ether with ligating donor atoms from the ring providing a full or partial inner coordination sphere for the metal ion. Crown-type compounds are of general relevance as synthetic model substances for study of physiological ion-transport processes in biological membranes, for investigation of receptor and enzyme interactions, as well as for the salt balance and also for metabolic processes of living organisms [3]. Crown ethers also have been utilized for separation of the metal cations [4, 5], in construction of ion selective electrodes [6, 7], and also in designing of optical sensors [8].

Studies of crown ethers complexation in different solvents show that the thermodynamic and kinetic parameters are affected by the nature and composition of the solvent system [9, 10]. A large number of physicochemical techniques such as potentiometry [11], calorimetry [12], conductometry [13], NMR spectrometry [14], spectrophotometry [15] and polarography [16, 17] have been used for study of complexation reactions between crown ethers with different metal cations in solutions.

Although the complexation reactions of crown ethers with metal cations have been studied in both aqueous and non-aqueous solvents, but the data about the stability of crown ether complexes in mixed solvents have been carried out only to a limited extent and little attention has been paid to these complexes particularly in mixed dipolar aprotic solvent systems such as acetonitrile–dimethylformamide binary solutions. In order to achieve appropriate solvent properties, we often use mixtures of two solvents. Mixed solvents play important roles in modern electrochemistry [18]. The use of mixed non-aqueous solvents in various fields of chemistry can contribute to advances in chemical science and can play an important role in finding new chemical possibilities.

The goal of the present investigation is to study the effect of nature of the cation, especially the solvent

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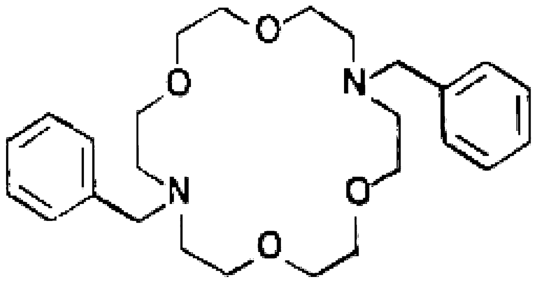

Scheme 1.

properties on the stability, selectivity and on thermodynamic parameters for complexation of 1,10-dibenzyl-1,10-diaza-18-crown-6 (DBDA18C6) (Scheme 1) with, Ni^{2+}, Cu^{2+}, Ag^{+}, and Cd^{2+} metal cations in acetonitrile–dimethylformamide (AN–DMF) binary systems at different temperatures using the conductometric method. The advantage of conductometry is that the measurements can be carried out at low solution concentrations, where the interactions between the cations and anions are known to be small. In addition, conductometry is a highly sensitive and inexpensive technique with a simple experimental arrangement.

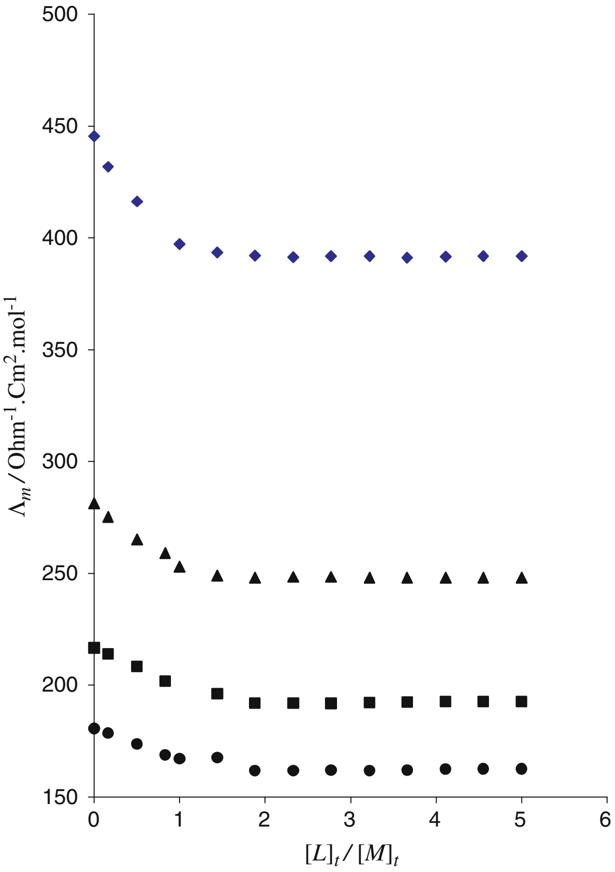

Figure 1. Molar conductance–mole ratio plots for DBDA18C6-Ag^{+} complex in AN–DMF binary system (mol%AN = 50) at different temperatures: (●) 45 °C, (■) 35 °C, (▲) 25 °C (♦), 15 °C.

Experimental

Reagents and solvents

1,10-Dibenzyl-1,10-diaza-18-crown-6 (Fluka), nikel(*II*) nitrate, mercury(*II*) nitrate, silver(I) nitrate and cadmium(*II*) nitrate all from Merck were used without further purification. The solvents: acetonitrile (Merck), dimethylformamide (Merck) were used with the highest purity.

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. Similar solution with the same total salt concentration was also used as solvent in the preparation of the DBDA18C6 solution (2.5×10^{-2} M). Then step-by-step increase in the crown ether concentration was carried out by a rapid transfer from crown ether solution 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 Metrohm conductivity apparatus (model 712) in a water bath (Julabo model F12) thermostated with a constant temperature maintained within ±0.01 °C. The

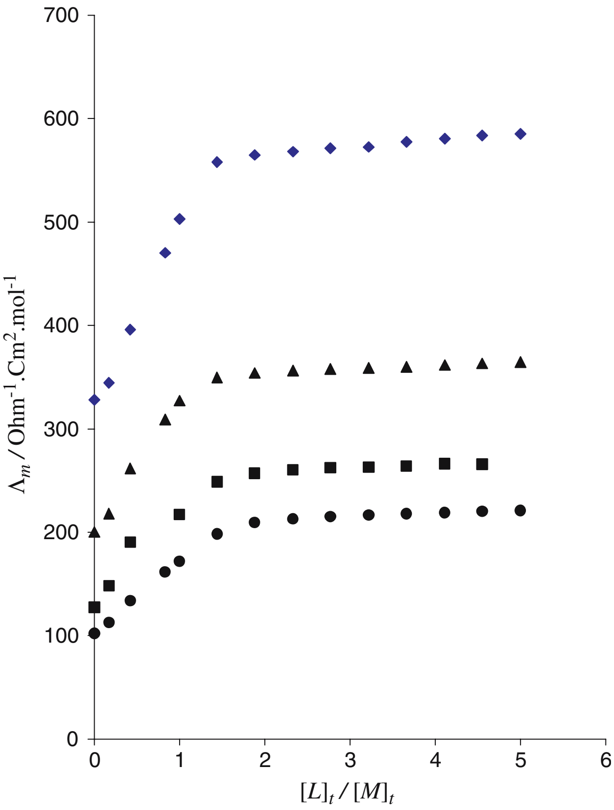

Figure 2. Molar conductance–mole ratio plots for DBDA18C6-Cd^{2+} complex in AN–DMF binary system (mol%AN = 96.6) at different temperatures: (●) 45 °C, (■) 35 °C, (▲) 25 °C, (♦) 15 °C.

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 1.25 cm^{-1} was used through the studies. The cell was calibrated with a standard solution of KCl (0.1000 M, Metrohm).

Results

The variations of molar conductance (Λ_m) versus the ligand to the cation molar ratio ($[L]_t/[M]_t$) for complexation of DBDA18C6 with Ni^{2+}, Cu^{2+}, Ag^{+} and Cd^{2+} metal cations in AN–DMF binary systems were studied at different temperatures. $[L]_t$ is the total concentration of the ligand and $[M]_t$ is the total concentration of the metal cation. Two typical series of molar conductance values versus the Ligand/Metal cation mole ratios in AN–DMF binary systems are shown in Figures 1 and 2. The stability constants of 1:1 complexes formed between DBDA18C6 and these heavy metal cations were calculated from the variation of the molar conductance as a function of Ligand/Metal cation mole ratio using a GENPLOT computer program [19]. The details of the calculation of the stability constants of complexes by the conductometric method have been described elsewhere [13]. The values of the stability constants (log K_f) for the DBDA18C6-M^{n+} ($M^{n+} = Ni^{2+}$, Cu^{2+}, Ag^{+} and Cd^{2+}) complexes in various solvent systems are listed in Table 1.

The 1:1 complexation of a metal cation, M^{n+} ($M^{n+} = Ni^{2+}$, Cu^{2+}, Ag^{+} and Cd^{2+}), with 1,10-dibenzyl-1,10-diaza-18-crown-6, L, is represented by the following equilibrium:

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

The corresponding equilibrium constant, K_f, is given by:

Table 1. Log K_f values of DBDA18C6-Ag^{+}, DBDA18C6-Ni^{2+}, DBDA18C6-Cd^{2+} and DBDA18C6-Cu^{2+} complexes in AN–DMF binary mixtures at different temperatures

Medium	Log K_f ± SD[a]			
	15 °C	25 °C	35 °C	45 °C
DBDA18C6-Ag^{+}[b]				
Pure AN	c	c	c	c
95.9%AN–4.1%DMF[d]	3.9 ± 0.1	4.10 ± 0.10	4.4 ± 0.3	4.5 ± 0.1
85.7%AN–14.3%DMF	5.6 ± 01	4.90 ± 0.04	4.4 ± 0.1	> 6
69.3%AN–30.7%DMF	4.5 ± 0.1	4.60 ± 0.10	4.3 ± 0.2	4.4 ± 0.2
50.0%AN–50.0%DMF	4.9 ± 0.1	4.10 ± 0.18	4.4 ± 0.2	4.4 ± 0.2
27.3%AN–72.7%DMF	4.50 ± 0.05	4.30 ± 0.20	4.4 ± 0.2	4.4 ± 0.2
Pure DMF	4.7 ± 0.1	4.80 ± 0.10	4.5 ± 0.1	4.3 ± 0.4
DBDA18C6-Ni^{2+}				
Pure AN	c	c	c	c
94.5%AN–5.5%DMF	3.1 ± 0.1	3.2 ± 0.3	3.5 ± 0.4	< 1
85.7%AN–14.3%DMF	3.5 ± 0.4	3.7 ± 0.1	4.2 ± 0.3	4.7 ± 0.3
60.0%AN–40.0%DMF	3.3 ± 0.2	3.5 ± 0.1	3.8 ± 0.2	3.6 ± 0.1
27.3%AN–72.7%DMF	3.8 ± 0.2	2.7 ± 0.1	2.8 ± 0.2	2.6 ± 0.1
Pure DMF	< 1	2.9 ± 0.4	3.2 ± 0.2	< 1
DBDA18C6-Cd^{2+}				
Pure AN	c	c	c	c
96.6%AN–3.4%DMF	4.2 ± 0.1	4.50 ± 0.05	4.0 ± 0.09	3.82 ± 0.09
82.5%AN–17.5%DMF	3.0 ± 0.1	2.80 ± 0.07	2.77 ± 0.09	2.30 ± 0.05
60.0%AN–40.0%DMF	3.3 ± 0.1	2.73 ± 0.28	3.20 ± 0.24	2.15 ± 0.15
27.3%AN–72.7%DMF	2.5 ± 0.3	2.10 ± 0.30	3.10 ± 0.20	2.30 ± 0.20
Pure DMF	< 1	< 1	< 1	< 1
BDA18C6-Cu^{2+}				
Pure AN	3.62 ± 0.21	3.61 ± 0.24	3.24 ± 0.15	3.97 ± 0.16
85.7%AN–14.3%DMF	2.24 ± 0.09	2.97 ± 0.10	2.19 ± 0.10	2.70 ± 0.06
69.3%AN–30.7%DMF	3.32 ± 0.24	2.88 ± 0.17	2.50 ± 0.10	2.53 ± 0.05
50.0%AN–50.0%DMF	3.50 ± 0.10	3.27 ± 0.17	3.05 ± 0.15	2.84 ± 0.09
27.3%AN–72.7%DMF	3.52 ± 0.05	3.61 ± 0.10	3.47 ± 0.14	2.90 ± 0.16
Pure DMF	3.50 ± 0.05	3.53 ± 0.05	3.52 ± 0.10	3.05 ± 0.12

[a] SD = standard deviation.

[b] The concentration of each metal cation was 5.0×10^{-4} M.

[c] The metal salts are not soluble.

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

$$K_f = \frac{[\mathrm{ML}^{n+}]}{[\mathrm{M}^{n+}][\mathrm{L}]}\frac{f_{\mathrm{ML}}{}^{n+}}{f_{\mathrm{M}}{}^{n+}f_{\mathrm{L}}}$$

where $[\mathrm{ML}^{n+}]$, $[\mathrm{M}^{n+}]$ and [L] denote the molar concentration of the complex, metal cation and crown ether and f indicates the activity coefficient of the species indicated. Under the highly dilute conditions which employed in these experiments, the $f_{\mathrm{ML}}{}^{n+}/f_{\mathrm{M}}{}^{n+}\ f_{\mathrm{L}}$ is essentially unity and, therefore, the equilibrium constants obtained in this study are thermodynamic equilibrium constants. The thermodynamic equilibrium constant, K_{f}, is related to Gibbs standard free energy of complexation reaction, $\Delta G°\mathrm{c}$. The van't Hoff plots of log K_{f} versus $1/T$ for all of the investigated systems were constructed.

The changes in the standard enthalpy ($\Delta H°\mathrm{c}$) for complexation reactions were obtained from the slope of the van't Hoff plots assuming that ΔC_{P} is equal zero over the entire temperature range investigated and the changes in standard entropy ($\Delta S°\mathrm{c}$) were calculated from the relationship $\Delta G°\mathrm{c}$, 298.15 = $\Delta H°\mathrm{c}$ $-298.15\Delta S°\mathrm{c}$. The thermodynamic data are summarized in Table 2. The changes of log K_{f} of DBDA18C6-Cu^{2+} complex versus the mole fraction of acetonitrile in AN–DMF binary systems at different temperatures are shown in Figure 3. The variations of log K_{f} for DBDA18C6-Ag^{+}, DBDA18C6-Cu^{2+}, DBDA18C6-Ni^{2+} and DBDA18C6-Cd^{2+} complexes versus ionic radii in different solvent systems are shown in Figure 4.

Discussion

As seen in Figure 1, addition of DBDA18C6, to silver ion in AN–DMF solution (mol%AN = 50) at different temperatures results in a decrease in molar conductivity which indicates that the DBDA18C6-Ag^{+} complex in AN–DMF binary system is less mobile than free solvated Ag^{+} cation. Similar behaviour was observed for DBDA18C6-Ni^{2+} complex in these binary solutions.

Table 2. Thermodynamic parameters for DBDA18C6-Ag^{+}, DBDA18C6-Ni^{2+}, DBDA18C6-$\mathrm{Cd}^{2+}$and DBDA18C6-Cu^{2+} complexes in AN–DMF binary mixtures

Medium	$-\Delta G°\mathrm{c} \pm \mathrm{SD}^{a}$ (KJ/mol)	$\Delta H°\mathrm{c} \pm$ SD (KJ/mol)	$\Delta S°\mathrm{c} \pm$ SD (J/mol K)
DBDA18C6-$\mathrm{Ag}^{+\,b}$			
Pure AN	c	c	c
95.9%AN–4.1%DMF[d]	−5.5 ± 0.2	7.9 ± 0.8	44.9 ± 2.6
85.7%AN–14.3%DMF	−6.6 ± 0.1	e	e
69.3%AN–30.7%DMF	−6.2 ± 0.2	−3.0 ± 1.8	11.0 ± 0.1
50.0%AN–50.0%DMF	−5.6 ± 0.2	−6 ± 1	1.3 ± 0.1
27.3%AN–72.7%DMF	−5.3 ± 0.5	~0	17.8 ± 0.1
Pure DMF	−6.5 ± 0.5	~0	21.8 ± 0.1
DBDA18C6-Ni^{2+}			
Pure AN	c	c	c
94.5%AN–5.5%DMF	−4.3 ± 0.3	8.5 ± 0.9	42.0 ± 3.0
85.7%AN–14.3%DMF	−5.1 ± 0.2	17.3 ± 1.2	75.1 ± 4.0
60.0%AN–40.0%DMF	−5.3 ± 0.4	−3.7 ± 0.6	5.4 ± 1.9
27.3%AN–72.7%DMF	−15.0 ± 0.1	1.79 ± 0.1	−50.8 ± 0.1
Pure DMF	13.2 ± 0.1	e	−44.4 ± 0.1
DBDA18C6-Cd^{2+}			
Pure AN	c	c	c
96.6%AN–3.4%DMF	−25.3 ± 1.0	−20.5 ± 2.6	10.1 ± 0.1
82.5%AN–17.5%DMF	−15.2 ± 0.3	−51.5 ± 2.4	121.8 ± 0.1
60.0%AN–40.0%DMF	−15.6 ± 1.5	−6.4 ± 0.3	42.7 ± 0.1
27.3%AN–72.2%DMF	11.98 ± 0.03	e	32.7 ± 0.2
DBDA18C6-Cu^{2+}			
Pure AN	20.6 ± 1.41	15.9 ± 1.9	e
85.7%AN–14.3%DMF	17.0 ± 0.5	11.1 ± 1.7	94.3 ± 5.4
69.3%AN–30.7%DMF	16.4 ± 0.9	−48.3 ± 2.5	−106.8 ± 7.6
50.0%AN–50.0%DMF	18.6 ± 1.0	−38.4 ± 6.3	−66.2 ± 0.6
27.3%AN–72.7%DMF	21.2 ± 0.6	−41.6 ± 1.1	−68.5 ± 2.9
Pure DMF	20.0 ± 0.4	21.3 ± 0.5	−4.4 ± 1.0

[a] SD = standard deviation.
[b] The concentration of each metal cation was 5.0×10^{-4}.
[c] The metal salts are not soluble.
[d] Composition of binary mixtures is expressed in mol% for each solvent system.
[e] With high uncertainity.

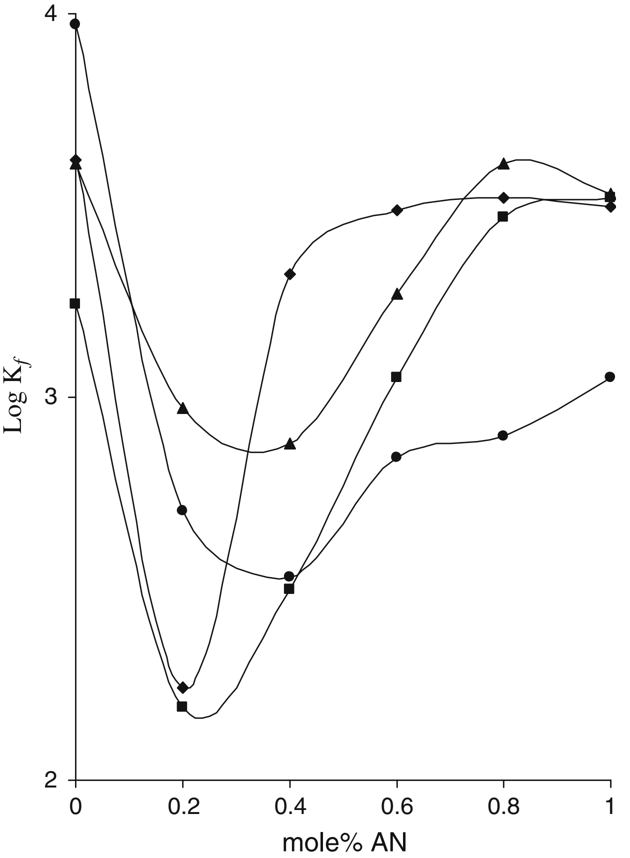

Figure 3. Changes of formation constant of DBDA18C6-Cu^{2+} complex with the composition of AN–DMF binary system at different temperatures: (●) 45 °C, (■) 35 °C, (▲) 25 °C, (♦) 15 °C.

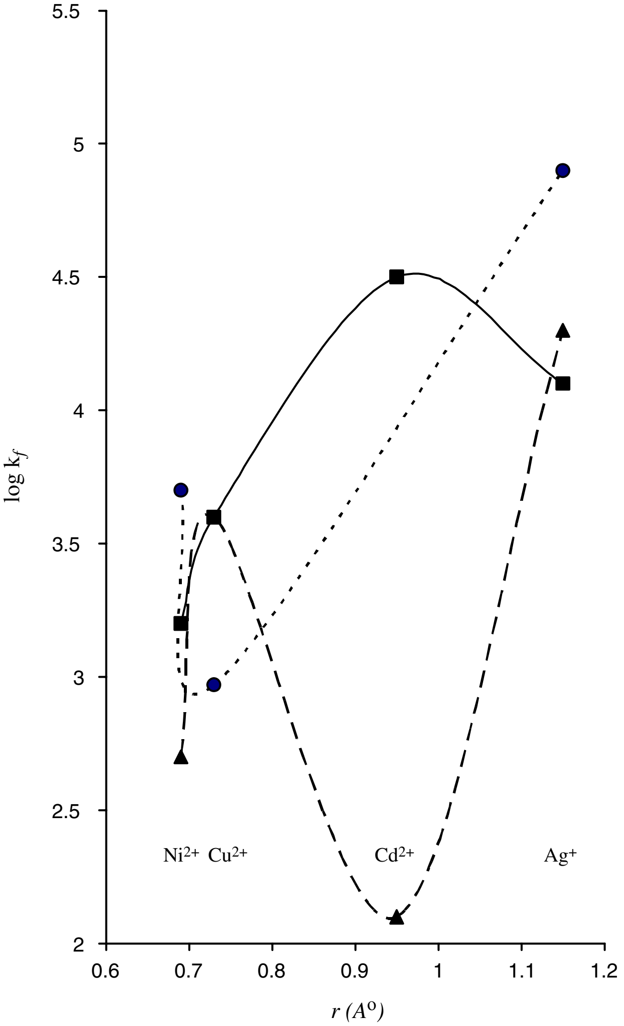

Figure 4. Changes of log K_f for DBDA18C6-Ag^+, DBDA18C6-Cu^{2+}, DBDA18C6-Ni^{2+} and DBDA18C6-Cd^{2+} complexes versus ionic radii in various solvent systems at 25 °C: (■) maximum mol% of AN, (●) mol%AN = 85.7, (▲) mol%AN = 27.3.

But as is evident in Figure 2, addition of DBDA18C6 to cadmium ion in AN–DMF binary system (mol%AN = 95) at different temperatures results in an increase in molar conductivity which indicates that the DBDA18C6-Cd^{2+} complex in this system is more mobile than free solvated Cd^{2+} cation. Similar behaviour was observed for DBDA18C6-Cu^{2+} complex. These behaviours can be explained on the basis of solvation sphere. It seems that the Ag^+ and Ni^{2+} metal ions are weakly solvated in these solvent systems. When these metal ions are complexed with large crown ether, DBDA18C6, they become bulkier causing a decrease in their mobility and also in molar conductivity values. The Cd^{2+} and Cu^{2+} ions, on the other hand, seems to be highly solvated in AN–DMF binary solutions. However, upon complexation, the crown ether molecule replaces the solvation sheath around the metal ions and as a result the moving entity becomes less bulky and more mobile.

As is shown in Figures 1 and 2, in all cases, the slope of the corresponding molar conductivity versus Ligand/Metal cation mole ratio plots changes sharply at the point where the ligand to cation mole ratio is about 1 which is an evidence for formation of a relatively stable 1:1 complexes between DBDA18C6 and these metal cations. It is evident from Figures 1 and 2 that the curvature of the plots of the DBDA18C6-Ag^+ and DBDA18C6-Cd^{2+} complexes decreases as the temperature increases, which indicates the formation of weaker complexes at higher temperatures. Therefore, the complexation reactions between Ag^+ and Cd^{2+} metal cations and DBDA18C6 ligand in these solvent systems are exothermic.

As is evident in Figure 3, the changes in the stability constant (log K_f) of DBDA18C6-Cu^{2+} complex versus the composition of AN–DMF binary solution is not monotonic. As the concentration of acetonitrile increases, the stability constant of the complex initially decreases very rapidly until the mole fraction of acetonitrile is reached to about 0.8 and then increases with the composition of the mixed binary system.

A non-linear behaviour was also observed for the other metal ion complexes in these binary mixed solvents systems. The non-linear behaviour which is observed for these complexation systems, may be due to heteroselective solvation of the metal cations and the ligand in these binary mixed solvents or it may be due to solvent–solvent interactions between these two solvent molecules which result in changing the structure of the solvent systems with their composition and, therefore, changing the solvation numbers of the metal cations, ligand and even the DBDA18C6-M^{n+} complexes in solutions. The interaction between AN and DMF molecules in AN–DMF binary solutions have been studied by viscosity and ultrasonic velocity measurements [20] and it has been shown that the values of compressibility and intermolecular free length are negative over the whole range of mole fraction, X of AN–DMF binary mixtures with a maximum at $X \sim 0.8$. The negative compressibility values show that there is a strong dipole–dipole interaction between the molecules of these dipolar aprotic solvents [21]. The acetonitrile and dimethylformamide both are dipolar aprotic liquids with large but nearly equal dipole moments [22, 23]. Thus mixing of dimethylformamide with acetonitrile will induce the mutual destruction of dipolar structures of component liquids and releasing free dipoles. As a result, strong dipolar interaction between acetonitrile and dimethylformamide molecules is expected.

The changes of log K_f for formation of DBDA18-C6-Ni^{2+}, DBDA18C6-Cu^{2+}, DBDA18C6-Ag^{+} and DBDA 18C6-Cd^{2+} complexes versus ionic radii in pure acetonitrile and acetonitrile–dimethylformamide binary solutions at 25 °C are shown in Figure 4. As is evident from this Figure, the sequence of stability of complexes of these heavy metal cations with DBDA18C6 ligand in AN–DMF binary solution (mol%AN = 27.3) is: $Ag^{+} > Cu^{+2} > Ni^{+2} > Cd^{+2}$. The Ag^{+} ion forms the most stable complex with DBDA18C6. This result is expected, because its ionic size (2.30 Å) is bigger than that of the other metal cations and it is very close to the size of the ligand's cavity (2.6–3.2 Å) and, therefore, it can attain more convenient fit condition than the other metal cations. In addition, the silver cation may also interact with the Pi electron system of the aromatic substituents present in the macrocyclic ligand [24].

As is evident from Figure 4, several reversals of stabilities are observed in the studied solvent systems. These reversals of stabilities indicate the possibility of changes in stabilities and, therefore, reversal of cation selectivities, which may be obtained in some selected mixed solvent systems.

As is evident from Table 2, the thermodynamics of complexation reactions between DBDA18C6 with Ni^{2+}, Cu^{2+}, Ag^{+} and Cd^{2+} metal cations is affected by the nature and composition of the mixed solvents and in most cases, the complexes are both enthalpy and entropy stabilized, therefore, the enthalpies and entropies of complexation reactions are the driving forces for formation of DBDA18C6-M^{n+} ($M^{n+} = Ni^{2+}, Cu^{2+}, Ag^{+}$ and Cd^{2+}) complexes. The experimental values of $\Delta H°c$ and $\Delta S°c$ (Table 2) show that the enthalpies and entropies of complexation reactions in acetonitrile–dimethylformamide binary solutions do not vary monotonically with the solvent composition. This behavior may reflect changes occurring in the structural distribution of the solvent molecules in the solvent mixtures which result in changing the interactions of AN and DMF molecules with the metal cations, ligand and even the resulting complexes. In addition, since there are many factors, which contribute to enthalpies and entropies of complexation reactions, therefore, we should not expect a monotonic relationship between these thermodynamic quantities and the solvent composition of the binary mixtures of these associated dipolar aprotic solvents.

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