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Study of Complex Formation Between Dicyclohexyl-18-Crown-6 with La^{3+}, UO_2^{2+}, Ag^+ and NH_4^+ Cations in Acetonitrile-Nitromethane Binary Mixtures

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The complexation processes of La^{3+}, UO_2^{2+}, Ag^+ and NH_4^+ cations with macrocyclic ligand, dicyclohexyl-18-crown-6 (DCH18C6) was studied in acetonitrile-nitromethane binary solutions at different temperatures using the conductometric method. The conductance data show that with the exception of complexation of NH_4^+ cation with this macrocyclic ligand, the stoichiometry of all the complexes which are formed in solutions, is 1:1 [M:L]. A different behaviour was observed in the case of complexation of NH_4^+ with DCH18C6 in which a 1:2 [$M:L_2$] complex is formed in solutions. A non-linear behaviour was observed for changes of log K_f of $(DCH18C6.La)^{3+}$, $(DCH18C6.UO_2)^{2+}$ and $(DCH18C6.Ag)^+$ complexes *versus* the composition of the binary mixed solvents. This behaviour may be related to hetero selective solvation of the cations and the ligand and also solvent-solvent interactions in these binary mixed solvent systems. The values of thermodynamic quantities (ΔH°_c, ΔS°_c) for formation of the complexes were obtained from temperature dependence of their stability constants using the van't Hoff plots. The results show that in all solvent systems, positive values of ΔS°_c characterize the formation of the complexes. The selectivity order of the ligand for the studied cations in pure acetonitrile and acetonitrile-nitromethane binary solutions (mol % AN = 50.0 and 75.0) was found to be $La^{3+} > UO_2^{2+} > Ag^+$.

Key Words: Dicyclohexyl-18-crown-6; La^{3+}, UO_2^{2+}, Ag^+, NH_4^+ cations, Acetonitrile-Nitromethane binary systems, Conductometry.

INTRODUCTION

Crown ethers are macrocyclic polyethers which form stable selective complexes with suitable cations. They were synthesized for the first time in 1967 with pioneering work of Pedersen[1]. The important characteristics of crown ethers are the number and type of donor atoms present in polyether ring, the dimension of the macrocycle cavity and the preorganization of the host molecule for most effective coordination. The so-called 'macrocyclic effect' of crown ethers is related to the last two characteristics.

Considerable researches have been carried out on a wide range of applications of these macrocyclic compounds in different areas such as designing of sensors[2], as stationary phase in chromatography columns[3-6], recognition of isomers[7], construction of ion-selective electrodes[8-11], separation of metal ions[12] and chemical analysis[13,14]. Most of applications of crown compounds are based on their complexing ability with various cations.

Understanding of the interactions between macrocyclic ligands and metal cations in solutions requires the study of various parameters governing the reactions. Thermodynamic studies of complexation reactions of crown ethers with metal ions result in important information on the thermodynamics of complexation reactions and also a better understanding of high selectivity of these ligands towards different metal cations in solutions. Various investigations have extensively studied thermodynamics of solution of macrocyclic polyether complexes during the past two decades[15-19] and Izatt and coworkers have compiled kinetic data[20].

Herein, we studied the complex formation between macrocyclic ligand, dicyclohexano-18-crown-6 (DCH18C6) with La^{3+}, UO_2^{2+}, Ag^+ and NH_4^+ cations in acetonitrile-nitromethane (AN/NM) binary systems at different temperatures using conductometric method. The purpose of the present work is to see how the stoichiometry and selectivity of the DCH18C6 complexes and also the thermodynamics of complexation reactions between these cations and the macrocyclic ligand are affected by the nature of the cations and the composition of the mixed non-aqueous acetonitrile-nitromethane binary solutions.

EXPERIMENTAL

DCH18C6(Merck), $La(NO_3)_3.6H_2O$(Merck), $UO_2(NO_3)_2.6H_2O$, $AgNO_3$ and NH_4NO_3 (all from Riedel) were used without further purification. Acetonitrile and nitromethane (Merck) were used with the highest purity.

The experimental procedure to obtain the stability constants of complexes is as follows: a solution of metal salt (1×10^{-4} M) was placed in a titration cell, thermostated at a given temperature and the conductance of the solution was measured. Then a step by step increase in the crown ether concentration was performed by a rapid transfer from crown ether solution prepared in the same solvent (2×10^{-3} M) to the titration cell using a microburett and the conductance of the solution in the cell was measured after each transfer at the desired temperature.

The conductance measurements were performed using a digital AMEL conductivity apparatus, model 60, in a water-bath thermostated at a constant temperature which maintained wihin ± 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 0.73 cm^{-1} was used throughout the studies.

RESULTS AND DISCUSSION

The variation of molar conductivity (Λ_m) *vs.* ligand to cation molar ratio ($[L]_t/[M]_t$) for the complexation of DCH18C6 with La^{3+}, UO_2^{2+}, Ag^+ and NH_4^+ cations in AN-NM binary systems were studied at different temperatures. $[L]_t$ and $[M]_t$ are the total concentrations of ligand and cations, respectively. The changes of Λ_m *vs.* $[L]_t/[M]_t$ for formation of $(DCH18C6.UO_2)^{2+}$ and $(DCH18C6.NH_4)^+$ complexes in a binary solution of acetonitrile-nitromethane (mol % AN = 50.0) are shown in Figs. 1 and 2, respectively.

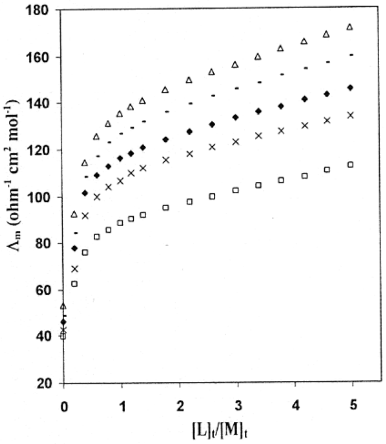

Fig. 1. Molar conductance-mole ratio plots for $(DCH18C6.UO_2)^{2+}$ complex in AN/NM binary systems (mol % AN = 50) at different temperatures (□ = 15 °C, × = 25 °C, ◆ = 35 °C, - = 45, Δ = 55 °C)

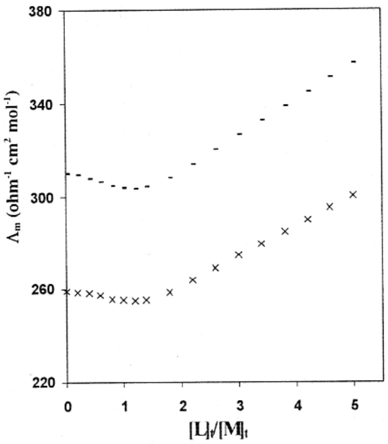

Fig. 2. Molar conductance-mole ratio plots for $(DCH18C6.NH_4)^+$ complex in AN/NM binary systems (mol % AN = 50) at two different temperatures (× = 25 °C, - = 45 °C)

The stability constants of the DCH18C6 crown ether complexes at each temprature were calculated from changes of the molar conductance as a function of $[L]_t/[M]_t$ molar ratios using a GENPLOT computer program[21]. The details of calculation of stability constants of complexes by conductometric method have been described by Rounaghi *et al.*[22]. The stability constants ($\log K_f$) for $DCH18C6.M^{n+}$(M^{n+} = La^{3+}, UO_2^{2+} and Ag^+) complexes in various solvent systems at different temperatures are given in Table-1. The van't Hoff plots of $\log K_f$ *vs.* 1/T for complexes were constructed. A typical example of these plots is shown in Fig. 3. The changes in the standard enthalpy (ΔH°_c) for complexation reactions were obtained from the slope of the van't Hoff plots and the changes in standard entropy (ΔS°_c) were calculated from the relationship $\Delta G^{\circ}_{c,298.15} = \Delta H^{\circ}_c - 298.15\ \Delta S^{\circ}_c$.

TABLE-1
log K_f VALUES OF $(DCH18C6.La)^{3+}$, $(DCH18C6.UO_2)^{2+}$ AND $(DCH18C6.Ag)^{+}$ COMPLEXES IN AN-NM BINARY MIXTURES AT DIFFERENT TEMPERATURES

Medium	log K_f ± SD[a]				
	15 °C	25 °C	35 °C	45 °C	55 °C
$(DCH18C6.La)^{3+}$					
Pure AN	4.88 ± 0.13	4.92 ± 0.13	4.90 ± 0.14	4.94 ± 0.14	4.88 ± 0.14
75%AN-25%NM[b]	4.73 ± 0.11	4.72 ± 0.11	4.67 ± 0.12	4.69 ± 0.12	4.71 ± 0.12
50%AN-50%NM	4.94 ± 0.13	4.89 ± 0.11	4.90 ± 0.12	4.83 ± 0.12	4.74 ± 0.11
25%AN-75%NM	c	c	c	c	c
Pure NM	c	c	c	c	c
$(DCH18C6.UO_2)^{2+}$					
Pure AN	4.78 ± 0.20	4.76 ± 0.21	4.78 ± 0.21	4.77 ± 0.24	4.74 ± 0.23
75%AN-25%NM[b]	4.66 ± 0.19	4.52 ± 0.16	4.99 ± 0.26	4.74 ± 0.24	4.65 ± 0.22
50%AN-50%NM	4.62 ± 0.21	4.82 ± 0.24	4.79 ± 0.26	4.79 ± 0.24	4.72 ± 0.23
25%AN-75%NM	4.79 ± 0.24	4.81 ± 0.21	4.68 ± 0.20	4.84 ± 0.28	4.84 ± 0.29
Pure NM	4.53 ± 0.20	4.42 ± 0.22	4.44 ± 0.22	4.38 ± 0.25	4.35 ± 0.28
$(DCH18C6.Ag)^{+}$					
Pure AN	2.74 ± 0.11	2.71 ± 0.11	2.70 ± 0.12	2.71 ± 0.12	2.72 ± 0.11
75%AN-25%NM[b]	2.77 ± 0.09	2.80 ± 0.08	2.72 ± 0.12	2.70 ± 0.13	2.74 ± 0.11
50%AN-50%NM	2.75 ± 0.10	2.73 ± 0.12	2.70 ± 0.14	2.69 ± 0.15	2.66 ± 0.17
25%AN-75%NM	2.82 ± 0.07	2.72 ± 0.12	2.69 ± 0.14	2.71 ± 0.12	2.62 ± 0.19
Pure NM	c	c	c	c	c

[a]SD=Standard deviation; [b]The composition of each mixed solvent system is experessed in mol % of each solvent; [c]The salts are not dissolved in these solvent systems.

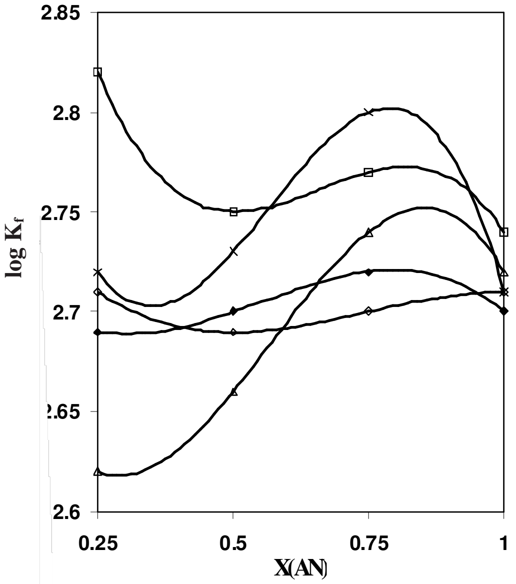

Fig. 3. Changes of stability constant of $(DB18C6.Ag)^{+}$ complex with the composition of the AN-NM binary system at different temperatures (□ = 15 °C, × = 25 °C, ♦ = 35 °C, ◊ = 45 °C, Δ = 55 °C)

The results are summarized in Table-2. The changes of log K_f of $(DCH18C6.Ag)^+$ complex *vs.* the mole fraction of AN in AN-NM binary systems at different temperatures is shown in Fig. 4. The changes of $\Delta S°_c$ for complexation processes *vs.* the solvent composition are shown in Fig. 5.

TABLE-2

THERMODYNAMIC PARAMETERS FOR $(DCH18C6.La)^{3+}$, $(DCH18C6.UO_2)^{2+}$ AND $(DCH18C6.Ag)^+$ COMPLEXES IN AN-NM BINARY MIXTURES

Medium	$-\Delta G^o_c \pm SD^a$ (25 °C) ($KJ\ mol^{-1}$)	$\Delta H^o_c \pm SD^a$ ($KJ\ mol^{-1}$)	$\Delta S^o_c \pm SD^a$ ($J\ mol^{-1}\ K^{-1}$)
$(DCH18C6.La)^{3+}$			
Pure AN	28.1 ± 0.8	c	94.25 ± 0.07
75%AN-25%NM[b]	26.9 ± 0.6	c	88.88 ± 0.05
50%AN-50%NM	27.9 ± 0.6	-2.5 ± 0.6	85.19 ± 0.01
$(DCH18C6.UO_2)^{2+}$			
Pure AN	27 ± 1	-0.4 ± 0.2	89.2 ± 0.1
75%AN-25%NM	25.8 ± 0.9	c	89.9 ± 0.3
50%AN-50%NM	28 ± 1	c	97.27 ± 0.01
25%AN-75%NM	27 ± 1	c	93.91 ± 0.01
Pure NM	25 ± 1	-2.1 ± 0.5	76.81 ± 0.09
$(DCH18C6.Ag)^+$			
Pure AN	15.5 ± 0.6	c	51.32 ± 0.06
75%AN-25%NM	16.0 ± 0.5	c	50.64 ± 0.04
50%AN-50%NM	15.6 ± 0.6	-1.2 ± 0.1	48.30 ± 0.06
25%AN-75%NM	15.5 ± 0.7	-2.2 ± 0.6	44.61 ± 0.04

[a]SD=Standard deviation; [b]The composition of each mixed solvent system is experessed in mol % of each solvent; [c]With high uncertainties.

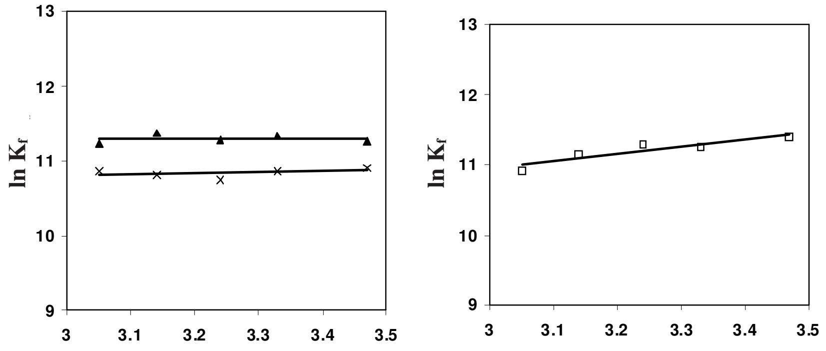

Fig. 4. Van't Hoff plots for $(DB18C6.La)^{3+}$ complex in AN-NM binary systems (mol % AN: × = 75.0, □ = 50.0, Δ = 25.0)

The variation of stability constants (log K_f) of $(DCH18C6.La)^{3+}$, $(DCH18C6.UO_2)^{2+}$ and $(DCH18C6.Ag)^{+}$ complexes as a function of cationic radii in AN/NM binary systems are shown in Fig. 6.

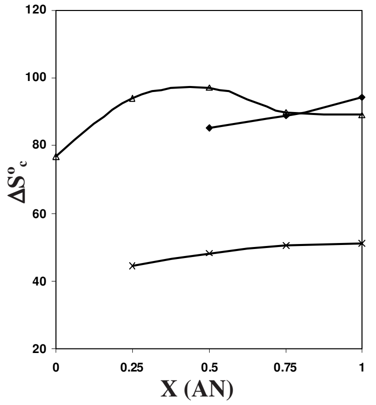

Fig. 5. Changes of $\Delta S°_c$ for $(DCH18C6.La)^{3+}$, $(DCH18C6.UO_2)^{2+}$ and $(DCH18C6.Ag)^{+}$ complexes with the composition of the AN-NM binary system ♦ $(DCH18C6.La)^{3+}$, Δ $(DCH18C6.UO_2)^{2+}$, × $(DCH18C6.Ag)^{+}$

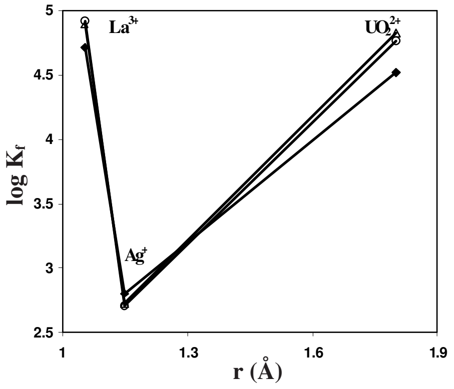

Fig. 6. Changes of log K_f for $(DCH18C6.La)^{3+}$, $(DCH18C6.UO_2)^{2+}$ and $(DCH18C6.Ag)^{+}$ complexes *vs.* cationic radii in various solvent systems at 25°C: (mol% AN: ♦ = 75.0, Δ = 50.0, × = 25.0)

As is seen from Fig. 1, addition of DCH18C6 ligand to UO_2^{2+} solution at different temperatures results in an increase in molar conductivity which indicates that the $(DCH18C6.UO_2)^{2+}$ complex is more mobile than free solvated UO_2^{2+} ion. Similar behaviour was observed for $(DCH18C6.La)^{3+}$ and $(DCH18C6.Ag)^{+}$ complexes in AN-NM binary solutions. The slope of the corresponding molar conductivity Λ_m *vs.* $([L]_t/[M]_t)$ plots changes sharply at the point where the ligand to cation molar ratio is about 1, which is an evidence for formation of a relatively stable 1:1 [M:L] complex between DCH18C6 and UO_2^{2+} cation in solution. Similar behaviour was observed for complexation of La^{3+} and Ag^{+} metal ions with the ligand in all solvent systems.

A different behaviour was observed for complexation of NH_4^+ cation with DCH18C6 in AN/NM binary systems. As is obvious from Fig. 2, addition of DCH18C6 to solution of NH_4^+ cation in AN/NM binary mixture (mol % AN = 50.0) at different temperatures, causes the molar conductivity to initially decrease until the molar ratio reaches to 1:1 and then to increase. Similar behaviour was observed for complexation of NH_4^+ in other AN/NM binary systems. Such behaviour may be described according to the following equilibria:

$$NH_4^+, NO_3^- \xleftrightarrow{DCH18C6} NH_4^+.DCH18C6, NO_3^- \qquad (1)$$

$$NH_4^+.DCH18C6, NO_3^- \xleftrightarrow{DCH18C6} NH_4^+(DCH18C6)_2 + NO_3^- \quad (2)$$

It seems that addition of the ligand to NH_4^+ cation solution results in formation of a relatively stable 1:1 complex (I) which is present as an ion-pair, then addition of the second ligand to ion-pair complex causes formation of a stable 1:2 [$M:L_2$] complex with a sandwich structure (II) which results in dissociation of ion-pair, therefore, the conductivity increases. Similar behaviour has been observed by Rounaghi and his coworkers in their study of complex formation between DB18C6 with Tl^+ ion in MeOH/AN binary mixture[23] and also for complexation of DCH18C6 with Sr^{2+} cation in methanol[24].

As is obvious from Fig. 3, the change of the formation constant (log K_f) of $(DCH18C6.Ag)^+$ complex with the mixed solvent composition of AN-NM binary mixtures at different temperatures is not linear. This behaviour may be due to strong interactions between the constituent solvent molecules which resulted changes in some of the chemical and physical properties of each of solvents. The structure of the solvent molecules also change when they mix with one another and therefore, changing their solvating ability towards the metal cations, ligand and the resulting complexes. A nonmonotic behaviour was also observed for $(DCH18C6.La)^{3+}$ and $(DCH18C6.UO_2)^{2+}$ complexes in these binary solutions.

As is evident from Table-2, the values of thermodynamic quantities for the complexation reactions vary with the composition of the mixed solvents. In all cases, the values of ΔS^o_c for the complexation reactions between DCH18C6 and La^{3+}, UO_2^{2+} and Ag^+ cations in AN-NM binary solutions are positive, therefore, the complexation reactions between DCH18C6 and the studied cations are entropy stabilized. It is reasonable to assume that the increase in entropy on complexation is due to additional solvent molecules which may be released from solvation shell of the studied cations upon complexation. It should be mentioned, however, that the complexation process involves not only a change in solvation of the cations, but also that of the ligand and the change in the flexibility of the ligand upon complexation. In addition, the solvent-solvent interactions contribute to changes in entropy. As indicated in Fig. 5, the values of ΔS^o_c for complexation of La^{3+} and Ag^+ metal ions with DCH18C6 increases monotonically with increasing the concentration of acetonitrile in acetonitrile-nitromethane binary solutions, but in the case of complexation of UO_2^{2+} with this ligand, a regular trend is not observed for variation of standard entropy changes with the solvent composition.

As shown in from Fig. 6, the selectivity order of DCH18C6 for La^{3+}, UO_2^{2+} and Ag^+ cations in pure AN and also in AN-NM binary systems (mol % AN = 50.0 and 75.0) at 25 °C is: $La^{3+} > UO_2^{2+} > Ag^+$.

The La^{3+} ion forms the most stable complex with DCH18C6. Since the charge density of La^{3+} metal ion is higher than that of UO_2^{2+} and Ag^+ cations and in addition La^{3+} cation acts as a harder acid than UO_2^{2+} and Ag^+ cations towards the oxygen donating atoms of the ligand which is a hard base, therefore, the interaction of La^{3+} cation with DCH18C6 ligand is stronger than that of the UO_2^{2+} and Ag^+ cations. The Ag^+ ion forms a weaker complex than UO_2^{2+} cations. This behaviour reflects the selective solvation of soft Ag^+ cation by acetonitrile molecule[25].

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