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Stabilities of Alkaline Earth Metal Ion Complexes with Dicyclohexano-18-Crown-6 in Acetonitrile-Water Binary Solutions

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Conductivities of alkaline earth metal salts in the presence of dicyclohexano-18-crown-6 (DCH18C6) were measured at different temperatures in acetonitrile-water (AN-H_2O) binary solutions. The stoichiometry of the complexes in most cases was found to be 1:1 (ML^{2+}), but in the case of complexation of Ca^{2+} and Ba^{2+} cations with DCH18C6 in pure acetonitrile, 1:2 (ML_2^{2+}) complexes are formed in solutions. Formation constants of 1:1 complexes (ML^{2+}) of DCH18C6 with Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} metal cations were determined using conductometric data. The results show that the stabilities and selectivities on complexation processes are governed by the solvent medium and the relative size of the metal cations and DCH18C6 cavity. An anomalous and interesting behaviour was observed for the case of complexation of Ca^{2+} and Ba^{2+} metal cations with the ligand in pure acetonitrile. In all cases, a non-linear behaviour was observed for variation of log K_f of the metal ion complexes *vs.* the composition of the acetonitrile-water binary solution. It was found that the selectivity order of DCH18C6 for the metal cations is changed in some composition of the mixed solvent. The values of thermodynamic quantities (ΔH°_c and ΔS°_c) for formation of complexes were obtained from temperature dependence of the formation constants of complexes using the van't Hoff plots. With the exception of complexation of Ca^{2+} ion with DCH18C6, the complexation reactions are enthalpy destabilized but entropy stabilized and the values of the thermodynamic parameters are influenced by the nature and composition of the mixed solvents.

Key Words: Dicyclohexano-18-crown-6, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} Metal cations, Acetonitrile-water binary mixtures, Conductometry.

INTRODUCTION

The effect of mixed solvent properties on the formation of crown ether-metal ion complexes is of interest due to the fact that the solvation capacities of crown ether molecules and metal ions change with changing the

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composition of the mixed solvents. Contrary to the wide range of information about complex formation between crown compounds and metal cations in pure organic solvents, the data in mixed solvents are spares[1-4].

The important characteristics of crown ethers are the number and type of donor atoms present in the polyether ring, the dimension of the macrocyclic cavity and the preorganization of the host molecule for the most effective coordination. The so-called 'macrocyclic effect' of crown ethers is related to the last two characteristics. Crown ethers are well known for their binding strength and selectivities towards alkali and alkaline earth metal cations[5,6].

Crown ethers form more or less stable complexes in the solution and vapour phase with a variety of organic and metalic cations. In these host-guest recognition processes, solvent plays a critical role in local structure optimization and complex stabilization. Thus, the complex stability is known to vary, sometimes drastically, according to the nature of solvent in which the reaction occurs[7]. Studies of crown ethers complexation in different solvents show that the thermodynamic and kinetic parameters depend on the nature and composition of the solvent systems[8,9].

Crown ethers are used in analytical separation, the recovery or removal of specific species present in solutions, in construction of ion selective electrodes, biological mimics and catalysis. Various physico-chemical techniques such as spectrophotometry[10], NMR spectrometry[11], calorimetry[12], potentiometry[13] and conductometry[14,15] have been reported to study the complex formation between crown ethers and various metal ions in solutions.

In this paper, we report the results of thermodynamic study for complexation reactions between DCH18C6 with Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} cations in AN-H_2O binary mixtures at different temperatures using conductometric method. Conductance measurements can be carried out easily and with high precision at very low concentrations. As a consequence, precise data can be obtained for a wide variaty of complexation systems at concentration for which theory is applicable.

EXPERIMENTAL

DCH18C6 (Fluka), magnesium nitrate (Merck), calcium nitrate (Analar), strontium nitrate (Merck) and barium nitrate (Merck) were used without further purification. Acetonitrile from Merck company and triply distilled water were used as solvents.

The conductance measurements were performed on an AMEL model 160 conductometer in a thermostated water-bath with a constant temperature maintained within ± 0.03 ºC. A conductometric cell with a cell constant of 0.74 cm^{-1} was used throughout the studies.

The experimental procedure to obtain the formation constants of complexes 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 the crown ether concentration was increased by adding crown ether solution in the same solvent (1.0×10^{-3} M) to the titration cell using a microburette and the conductance of the resulted solution was measured after each step at the desired temperature.

RESULTS AND DISCUSSION

The variation of molar conductivity, Λ_m, *vs.* the ligand to metal cation mole ratio ($[L]_t/[M]_t$) for the complexation of DCH18C6 with Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} cations in acetonitrile-water (AN-H_2O) binary systems were studied at different temperatures. Two typical series of molar conductance values as a function of $[L]_t/[M]_t$ for $(DCH18C6\text{-}Sr)^{2+}$ and $(DCH18C6\text{-}Ca)^{2+}$ in pure AN are shown in Figs. 1 and 2, respectively.

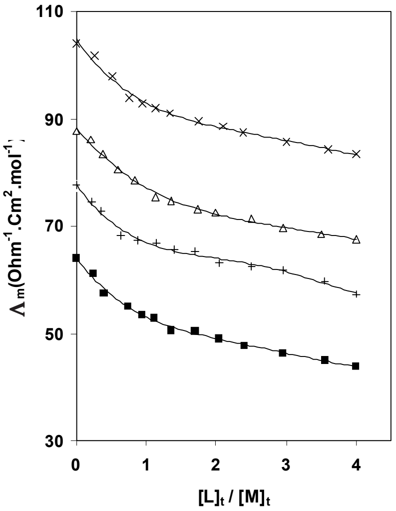

Fig. 1. Molar conductance-mole ratio plots for $(DCH18C6\text{-}Sr)^{2+}$ complex in pure acetonitrile at different temperatures (■ 15 ºC, + 25 ºC, Δ 35ºC, × 45 ºC)

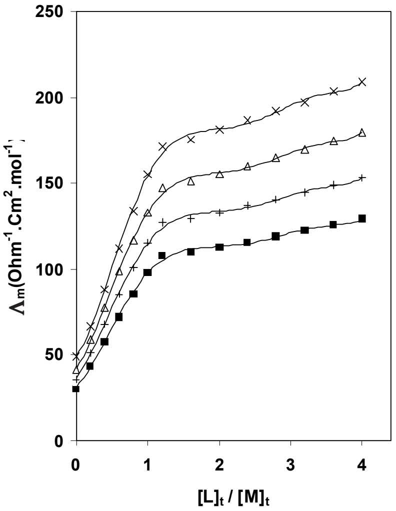

Fig. 2. Molar conductance-mole ratio plots for $(DCH18C6\text{-}Ca)^{2+}$ complex in pure acetonitrile at different temperatures (■ 15 ºC, + 25 ºC, Δ 35 ºC, × 45 ºC)

The formation constants of the complexes at each temperature were obtained from variation of molar conductance *vs.* the [Ligand]/[M^{2+}] molar ratio plots using a GENPLOT computer program[16]. The details of calculation of the stability constants of complexes by conductometric method have been described in reference[17]. The values of the formation constants (log K_f) for the $(DCH18C6\text{-}M)^{2+}$ ($M^{2+} = Mg^{2+}$, Ca^{2+}, Sr^{2+} and

Ba^{2+}) complexes in various solvent systems are listed in Table-1. Plots of Ln K_f *vs.* 1/T in all cases were linear and a typical example of these plots is shown in Fig. 3.

TABLE-1
log K_f VALUES OF $(DCH18C6\text{-}Mg)^{2+}$, $(DCH18C6\text{-}Ca)^{2+}$, $(DCH18C6\text{-}Sr)^{2+}$ AND $(DCH18C6\text{-}Ba)^{2+}$ COMPLEXES IN AN-H_2O BINARY MIXTURES AT DIFFERENT TEMPERATURES

Medium	log K_f ± SD[a]			
	15 °C	25 °C	35 °C	45 °C
$(DCH18C6\text{-}Mg)^{2+}$ [b]				
Pure AN	2.93 ± 0.07	3.02 ± 0.04	3.20 ± 0.03	3.25 ± 0.03
64% AN-36% H_2O [c]	2.94 ± 0.04	2.99 ± 0.01	3.02 ± 0.02	3.04 ± 0.00
30.6% AN-69.4% H_2O	3.04 ± 0.03	3.06 ± 0.03	3.10 ± 0.08	3.15 ± 0.05
13.7% AN-86.3% H_2O	2.76 ± 0.06	2.94 ± 0.04	3.07 ± 0.04	3.14 ± 0.05
Pure H_2O	3.03 ± 0.06	3.05 ± 0.06	3.07 ± 0.06	3.11 ± 0.07
$(DCH18C6\text{-}Ca)^{2+}$ [b]				
64% AN-36% H_2O [c]	3.17 ± 0.04	3.09 ± 0.01	3.04 ± 0.04	3.01 ± 0.09
30.6% AN-69.4% H_2O	3.16 ± 0.05	3.07 ± 0.05	2.99 ± 0.06	2.95 ± 0.07
13.7% AN-86.3% H_2O	3.12 ± 0.03	3.04 ± 0.02	2.93 ± 0.05	2.80 ± 0.11
Pure H_2O	3.10 ± 0.06	3.02 ± 0.07	3.00 ± 0.02	2.95 ± 0.07
$(DCH18C6\text{-}Sr)^{2+}$ [b]				
Pure AN	4.07 ± 0.11	4.12 ± 0.18	4.16 ± 0.07	4.19 ± 0.11
64% AN-36% H_2O [c]	2.25 ± 0.39	2.91 ± 0.06	3.07 ± 0.02	3.31 ± 0.05
30.6% AN-69.4% H_2O	3.09 ± 0.04	3.22 ± 0.03	3.31 ± 0.03	3.38 ± 0.06
13.7% AN-86.3% H_2O	3.40 ± 0.03	3.34 ± 0.01	3.30 ± 0.01	3.26 ± 0.04
Pure H_2O	2.97 ± 0.02	3.21 ± 0.15	3.45 ± 0.06	3.72 ± 0.05
$(DCH18C6\text{-}Ba)^{2+}$ [b]				
64% AN-36% H_2O [c]	2.48 ± 0.22	2.83 ± 0.30	2.93 ± 0.02	3.08 ± 0.03
30.6% AN-69.4% H_2O	3.52 ± 0.03	3.57 ± 0.01	3.60 ± 0.02	3.64 ± 0.02
13.7% AN-86.3% H_2O	3.66 ± 0.03	3.72 ± 0.02	3.76 ± 0.06	3.78 ± 0.08
Pure H_2O	3.71 ± 0.08	3.79 ± 0.06	3.83 ± 0.06	3.88 ± 0.07

[a] SD = standard deviation.

[b] The concentration of each metal cation was 1.0×10^{-4} M.

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

The changes in the standard enthalpy (ΔH°_c) for complexation reactions were determined in the usual manner from the slope of the van't Hoff plots assuming that ΔC_p is equal to zero over the entire temperature range investigated. The changes in standard entropy (ΔS°_c) were calculated from the relationship: $\Delta G^\circ_{c,298.15} = \Delta H^\circ_c - 298.15\ \Delta S^\circ_c$. The results are summarized in Table-2.

The changes of log K_f *vs.* the mole fraction of AN for $(DCH18C6\text{-}M)^{2+}$ complexes in AN-H_2O binary systems at 25 °C is shown in Fig. 4 and the changes of log K_f of DCH18C6 complexes with Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} metal cations *vs.* cationic diameter in AN-H_2O binary solutions at 25 °C is shown in Fig. 5.

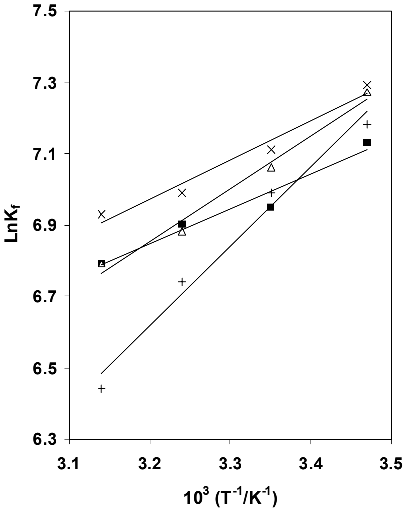

Fig. 3. Van't Hoff plots for $(DCH18C6\text{-}Ca)^{2+}$ in AN-H_2O binary systems (mol %AN: ■ 0.0, + 13.7, Δ 30.6, × 64.0)

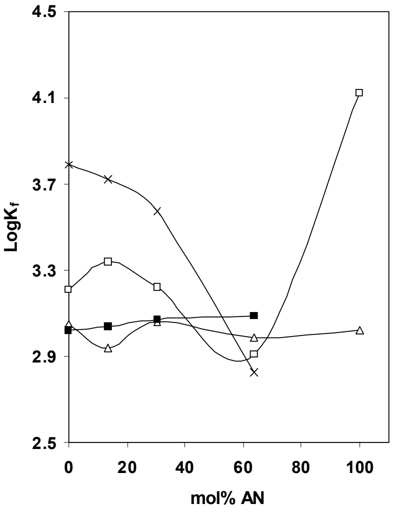

Fig. 4. Changes of stability constants of $(DCH18C6\text{-}M)^{2+}$ complexes with the mole fraction of AN at 25 ºC (Δ Mg^{2+}, ■ Ca^{2+}, □ Sr^{2+}, × Ba^{2+})

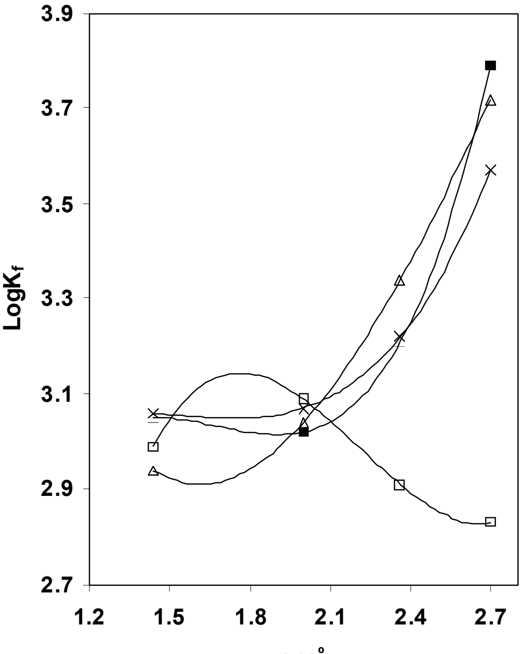

Fig. 5. Changes of log K_f of DCH18C6 complexes of Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} at 25 ºC *vs.* cationic diameter (mol% AN: ■ 0.0, Δ 13.7, × 30.6, □ 64.0)

TABLE-2
THERMODYNAMIC PARAMETERS FOR $(DCH18C6\text{-}Mg)^{2+}$, $(DCH18C6\text{-}Ca)^{2+}$, $(DCH18C6\text{-}Sr)^{2+}$ AND $(DCH18C6\text{-}Ba)^{2+}$ COMPLEXES IN AN-H_2O BINARY MIXTURES

Medium	$-\Delta G^o_c \pm SD^a$ (25 °C) (Kcal/mol)	$\Delta H^o_c \pm SD^a$ (Kcal/mol)	$\Delta S^o_c \pm SD^a$ (cal/mol.K)
$(DCH18C6\text{-}Mg)^{2+\,b}$			
Pure AN	4.16 ± 0.17	4.76 ± 0.76	29.91 ± 2.69
64% AN-36% H_2O [c]	4.07 ± 0.04	1.39 ± 0.18	18.31 ± 0.55
30.6% AN-69.4% H_2O	4.19 ± 0.13	1.54 ± 0.23	19.23 ± 0.77
13.7% AN-86.3% H_2O	3.98 ± 0.16	5.35 ± 0.67	31.27 ± 2.19
Pure H_2O	4.16 ± 0.25	1.09 ± 0.15	17.62 ± 0.53
$(DCH18C6\text{-}Ca)^{2+\,b}$			
64% AN-36% H_2O [c]	4.23 ± 0.04	-2.23 ± 0.29	6.71 ± 1.01
30.6% AN-69.4% H_2O	4.19 ± 0.15	-2.91 ± 0.41	4.29 ± 1.41
13.7% AN-86.3% H_2O	4.13 ± 0.08	-3.98 ± 0.28	0.52 ± 0.08
Pure H_2O	4.15 ± 0.29	-1.76 ± 0.21	8.03 ± 0.84
$(DCH18C6\text{-}Sr)^{2+\,b}$			
Pure AN	5.62 ± 0.95	1.68 ± 0.12	24.47 ± 0.49
64% AN-36% H_2O [c]	3.72 ± 0.22	14.15 ± 2.97	59.93 ± 3.95
30.6% AN-69.4% H_2O	4.37 ± 0.13	4.04 ± 0.34	28.21 ± 1.13
Pure H_2O	4.40 ± 0.66	10.32 ± 0.31	49.35 ± 0.99
$(DCH18C6\text{-}Ba)^{2+\,b}$			
64% AN-36% H_2O [c]	3.74 ± 1.12	8.04 ± 1.45	39.50 ± 3.74
30.6% AN-69.4% H_2O	4.86 ± 0.05	1.64 ± 0.07	21.81 ± 0.22
13.7% AN-86.3% H_2O	5.06 ± 0.10	1.69 ± 0.24	22.63 ± 0.91
Pure H_2O	5.15 ± 0.31	2.32 ± 0.19	25.05 ± 0.75

[a] SD = standard deviation.

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

As is evident from Fig. 1, addition of DCH18C6 to Sr^{2+} ion in pure acetonitrile at different temperatures shows a decrease in molar conductivity. This indicates that DCH18C6 forms a complex with Sr^{2+} cation in this solvent and the complex is less mobile than free solvated Sr^{2+} ion. Similar behaviour was observed for Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} metal ion complexes in various AN-H_2O binary solutions. The slop of the corresponding molar conductivity *vs.* ligand/cation mole ratio 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 1:1 complex in solution.

Although the formation constant of $(DCH18C6\text{-}Ca)^{2+}$ complex decreases with increasing the temperature (Table-1) and therefore, there is an exothermic reaction between Ca^{2+} metal ion with DCH18C6 in AN-H_2O binary solutions. But as evident from Table-1, the formation constants of $(DCH18C6\text{-}Mg)^{2+}$, $(DCH18C6\text{-}Sr)^{2+}$ and $(DCH18C6\text{-}Ba)^{2+}$ complexes increase with increasing the temperature, therefore, the complexation reactions between Mg^{2+}, Sr^{2+} and Ba^{2+} metal cations with the ligand in these binary mixed solutions are endothermic.

The molar conductance-mole ratio plots for (DCH18C6-Ca^{2+}) complex in pure acetonitrile at different temperature are shown in Fig. 2. It is interesting to note that as the DCH18C6/Ca^{2+} mole ratio increases from 0 to 1, the molar conductivity increases sharply, then further addition of the ligand, results in a gradual increase in molar conductivity. Somewhat, similar behaviour was observed for complexation of Ba^{2+} cation with DCH18C6 in pure acetonitrile.

It seems that the nitrate salts of Ca^{2+} and Ba^{2+} metal cations are present as ion-pair in pure acetonitrile solutions. Therefore, we may suggest that the nitrate ion is released in two steps according to the following equations:

$$(M^{2+}\cdot 2NO_3^-) + L \longrightarrow (ML^{2+}\cdot NO_3^-) + NO_3^- \quad \text{(I)}$$

$$(ML^{2+}\cdot NO_3^-) + L \longrightarrow (ML_2^{2+}) + NO_3^- \quad \text{(II)}$$

$(M^{2+} = Ca^{2+}, Ba^{2+})$; (L = DCH18C6)

In the first step, DCH18C6 forms 1:1 $(ML)^{2+}$ complexes with Ca^{2+} and Ba^{2+} cations which are present as ion-pairs (I), then further addition of the ligand to the acetonitrile solutions, results in releasing the second nitrate anion and therefore, formation of 1:2 $(ML_2)^{2+}$ complexes (II). The results obtained in this investigation show that the stiochiomtry of the crown ether-metal cation complexes may change with the nature and composition of the mixed solvent systems.

The changes of formation constants of $(DCH18C6\text{-}Mg)^{2+}$, $(DCH18C\text{-}Ca)^{2+}$, $(DCH18C6\text{-}Sr)^{2+}$ and $(DCH18C6\text{-}Ba)^{2+}$ complexes *vs.* the mole fraction of acetonitrile in acetonitrile-water binary solutions at 25 ºC are shown in Fig. 4. As is evident in this Figure, a non-linear relationship is observed between log K_f of the complexes with the composition of the mixed solvent. This behaviour may be due to interaction between the water and acetonitrile molecules *via* hydrogen bonding in their binary mixtures which results in changing the structure of the mixed solvents and therefore, changing the solvation of the alkaline earth metal cations, the ligand and the resulting $(DCH18C6\text{-}M)^{2+}$ complexes in AN-H_2O binary solutions. In addition, the preferential solvation of the studied metal cations in these binary solutions may affect complexation processes.

The changes of formation constants (log K_f) of $(DCH18C6\text{-}Mg)^{2+}$, $(DCH18C6\text{-}Ca)^{2+}$, $(DCH18C6\text{-}Sr)^{2+}$ and $(DCH18C6\text{-}Ba)^{2+}$ complexes versus the ionic diameter in AN-H_2O binary mixtures at 25ºC is shown in Fig. 5. As is evident from Fig. 5, for most solvent compositions the sequence of stabilities of these metal ion complexes is: $(DCH18C6\text{-}Ba)^{2+}$ > $(DCH18C6\text{-}Sr)^{2+}$ > $(DCH18C6\text{-}Ca)^{2+}$ > $(DCH18C\text{-}Mg)^{2+}$.

The selectivity of crown ethers for metal cations is explained in terms of size-fit concept that a crown ether forms a more stable complex with the cation which is more suitable in size for the crown ether cavity. Since the ionic size of Ba^{2+} ion (2.72 Å)[18] is very close to the cavity size of DCH18C6 (2.6-3.2 Å)[19], it forms the most stable complex. The size of Sr^{2+} ion (2.26 Å) is relatively close to the cavity size of the ligand, but since the ionic sizes of Ca^{2+} (2.00 Å) and Mg^{2+} (1.92 Å) cations are smaller than the DCH18C6 cavity, therefore, they form less stable complexes with this ligand.

As is obvious from Fig. 5, some reversals in stabilities are observed in some compositions of the acetonitrile-water binary solutions. These reversals of stabilities show the possibility of changes in cation selectivities of the crown ethers which may be obtained in a selected mixed solvent system.

The results obtained in this study show that the sequence of stabilities and selectivities on complexation process between DCH18C6 and the alkaline earth metal cations in AN-H_2O binary solvents are apparently governed by the relative size of the metal cations and DCH18C6 cavity and the solvent effect. Therefore, it seems that in addition to the size fit condition, the solvation energies of the metal cations, ligand and even the resulting complexes are also effective upon these complexation reactions in acetonitrile-water binary solutions.

As illustrated in Table-2, the enthalpy and entropy values for complexation reactions vary with the nature and composition of the mixed solvents. The experimental values of ΔH^{o}_{c} and ΔS^{o}_{c} show that with the exception of $(DCH18C6\text{-}Ca)^{2+}$, all of the complexes are enthalpy destabilized but entropy stabilized, therefore, the entropies of complexation reactions are the principal driving forces for formation of these complexes in acetonitrile-water binary solutions.

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