

Effect of solvent on the stability constant of complex formation and the thermodynamic parameters between dicyclohexyl-18-crown-6 with Eu^{3+} , La^{3+} , Er^{3+} and Y^{3+} cations

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Abstract The complexation reaction between Eu^{3+} , La^{3+} , Er^{3+} and Y^{3+} cations with the dicyclohexyl-18-crown-6 (DCH18C6) in acetonitrile (AN)–dimethylformamide (DMF) and AN–methanol (MeOH) binary systems have been studied at different temperatures using conductometric method. The conductometric data show that the stoichiometry of the complexes is 1:1 [ML]. The results show that the stability constant of complexes in various solvents is: AN > MeOH > DMF. In the some cases, the minimum of $\log K_f$ for (DCH18C6– Eu^{3+}), (DCH18C6– La^{3+}), (DCH18C6– Er^{3+}) and (DCH18C6– Y^{3+}) complexes in AN–MeOH binary systems obtain at $\chi_{\text{MeOH}} \sim 0.75$, and also, the $\log K_f$ of (DCH18C6– Er^{3+}) complex in AN–DMF binary systems show a minimum at $\chi_{\text{AN}} \sim 0.75$. Non-linear behavior was observed for the stability constant of complexes versus the composition of the solvent systems. The experimental data show that the selectivity order of DCH18C6 for these cations in AN–MeOH binary systems (mol% AN = 50, 75) at 25 °C is: $\text{Y}^{3+} > \text{Er}^{3+} > \text{Eu}^{3+} > \text{La}^{3+}$. The values of thermodynamic parameters ($\Delta \dot{H}_C$) for formation of complexes were obtained from temperature dependence of stability constants of complexes using the van't Hoff plots and the standard entropy ($\Delta \dot{S}_C$) were calculated from the relationship: $\Delta \dot{G}_C, 298.15 = \Delta \dot{H}_C - 298.15 \Delta \dot{S}_C$. The results show that the values of these thermodynamic parameters are influenced by the nature and the composition of the binary systems.

Keywords Eu^{3+} , La^{3+} , Er^{3+} and Y^{3+} cations · AN–DMF · AN–MeOH · Binary systems · Conductometric · Thermodynamic parameters

Introduction

Rare earth of elements (REE) have been used extensively in igneous, sedimentary and metamorphic petrology to trace source of rocks and minerals during crustal and mantle evolution [1, 2]. The trace amounts of such metals can contaminate the surrounding watershed and ecosystem [3], representing a serious threat to human health and local ecosystems, e.g. through accumulation of metals in food chains [4]. Commercial fertilizers have been used for decades and will probably continue to be used for many decades to come. Hence, even low annual accumulation may finally build up concentrations in soil, especially where fertilizers with high heavy metal or rare earth element concentrations are used. Industrial use of REE, however, increased about 50 times the world over during the last 40 years [5].

Generally, the techniques employed for REE removal include precipitation [6], ion exchange, adsorption, filtration, liquid–liquid extraction [7], and reverse osmosis [8]. However most of them do not lead to a satisfactory depollution considering the operational costs [9]. Precipitation methods are particularly reliable but require large settling tank for the precipitation of voluminous alkaline sludge and a subsequent treatment is needed. Ion exchange has the advantage of allowing the recovery of metallic ions [10, 11], but it is expensive and sophisticated.

Pederson [12] published the first report on crown compounds in 1967. Since then, considerable research has been carried out on a wide range of applications of these compounds in different areas such as organic synthesis, polymer synthesis and separation metals ions. Although the complexation reactions of crown ethers with REE have been studied in both aqueous and non-aqueous solvents, the data about the stability of crown ether complexes in mixed

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solvents have been carried out only to a limited extent and little attention has been carried paid to these complexes particularly in mixed dipolar aprotic solvent systems such as AN–DMF binary mixtures.

Due to the specific affinity of rare metals and metal complexing group (e.g. crown ether), the thermal and chemical stability of these complexes needs further improvements.

In fact, the long-standing interest in all mixed solvents is largely due to their importance as tunable reaction media. The dielectric constant and relaxation time, excess adiabatic compressibility, excess intermolecular free length, excess volume, excess viscosity, as well as the refractive indexes and other transport properties of binary solvents, can be conveniently tuned by changing the composition [13–15].

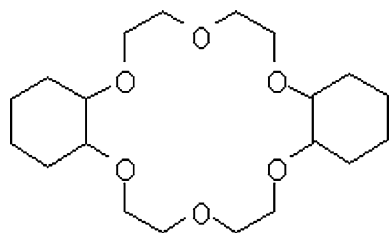
The effect of mixed solvent properties on the formation of crown ether–metal cation complexes is of interest due to that the solvation capacities of crown ether molecules and cations change with changing the mixed solvent composition on the other hand; the species are solvated competitively by the constituted solvents. The effects of mixed solvent properties on the formation of the crown ether complexes have been studied to a very limited extent.

In this work, we studied the complex formation between dicyclohexyl-18-crown-6 (DCH18C6) (Scheme 1) with Eu^{3+} , La^{3+} , Er^{3+} and Y^{3+} cations in AN–DMF and AN–MeOH binary systems were studied using conductometric method.

Material and experimental procedures

Dicyclohexyl-18-crown-6 (DCH18C6) (a mixture of cis and trans) (Merck), lanthanum chloride ($\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$) (Analar), iridium nitrate [$\text{Ir}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$], europium nitrate [$\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$] (Riedel), Yttrium nitrate [$\text{Y}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$] (Merck) were used without further purification. AN, MeOH and N, N-DMF (all from Merck) were used with the highest purity.

The experimental procedure to obtain the formation constants of complexes is as follow: a solution of metal salt (5×10^{-4} M) was placed in a titration cell and conductance



Scheme 1

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 (2×10^{-3} M) to the titration cell and the conductance of the solution in the cell was measured after each transfer at the desired temperature. The conductance measurements were performed on a digital El Metron conductivity apparatus, model cc-411, in a water-bath thermostated at a constant temperature maintained within of ± 0.1 °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 0.94 cm^{-1} was used throughout the studies.

Results

The changes of molar conductivity (Λ_m) versus the ligand to cation mole ratio for the complexation of dicyclohexyl-18-crown-6 with Eu^{3+} , La^{3+} , Er^{3+} and Y^{3+} cations in AN–DMF and AN–MeOH binary systems were studied at different temperatures.

Two typical examples molar conductance–mole ratio are shown in Figs. 1 and 2. The stability constants ($\log K_f$)

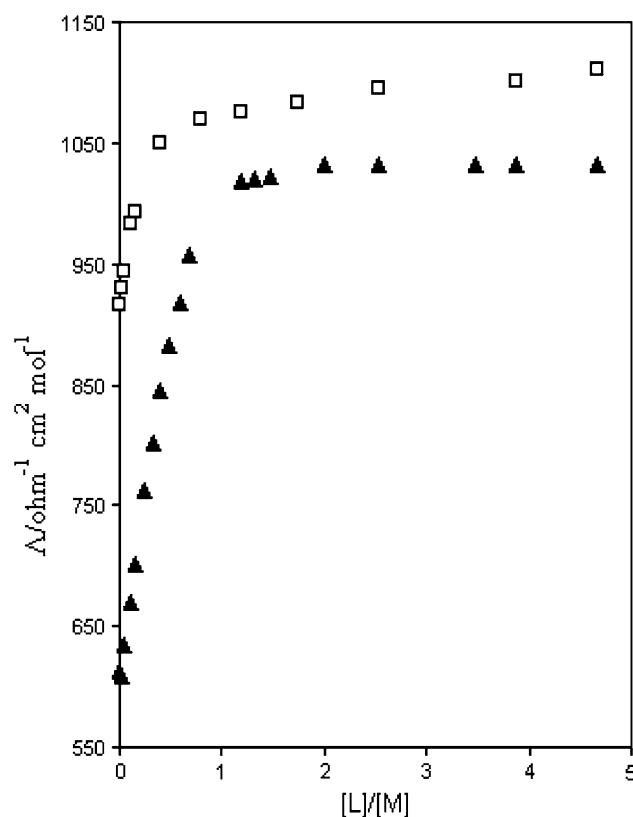


Fig. 1 Molar conductance–mole ratio plots for (DCH18C6– La^{3+}) complex in AN–DMF (mol% AN = 50) binary systems at 25 °C (filled triangle) and 45 °C (empty square)

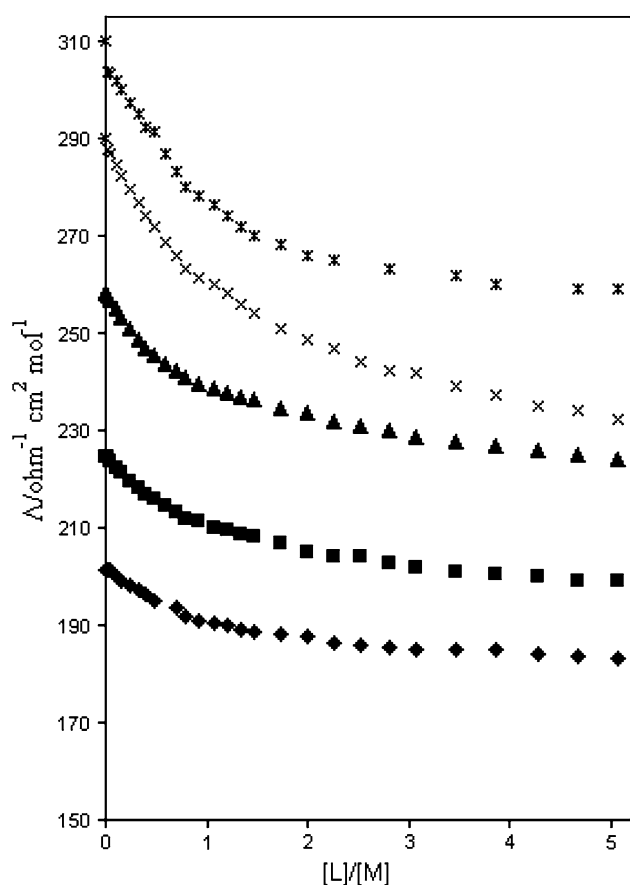


Fig. 2 Molar conductance–mole ratio plots for (DCH18C6–Y³⁺) complex in AN–DMF (mol% AN = 50) binary systems 15 °C (filled diamond), 25 °C (empty square), 35 °C (filled triangle), 45 °C (times) and 55 °C (asterick)

for DCH18C6–M³⁺ (M³⁺ = Eu³⁺, La³⁺, Er³⁺, Y³⁺) complexes in various solvent systems are listed in Tables 1 and 2. The details of calculation of stability constant of complexes have been described earlier [16].

The changes in standard enthalpy (ΔH°_c) for the complexation reactions were determined in the usual manner from the slopes of the van't Hoff plots, and the changes in standard entropy (ΔS°_c) were calculated from the relationship: ΔG°_c, 298.15 = ΔH°_c – 298.15ΔS°_c. The results are summarized in Tables 3 and 4. A typical of example of the van't Hoff plots is shown in Fig. 3.

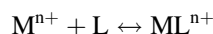
Discussion

The addition of DCH18C6 ligand to both the solution of Eu³⁺ cation with 25 mol% AN and the La³⁺ cation with 50 and 75 mol% AN in AN–DMF binary systems at different temperatures shows that the molar conductivity values increase with increasing [DCH18C6]_t/[M]_t mole ratio. This

indicates that (DCH18C6–Eu³⁺) and (DCH18C6–La³⁺) complexes in these binary systems have higher mobility than free solvated Eu³⁺ and La³⁺ cations (Fig. 1). On the other hand, a decrease to 1:1 mole ratio in the molar conductivity values was observed when DCH18C6 ligand was added to solution of Er³⁺ and Y³⁺ cations in all mol% AN and 25 mol% AN for La³⁺ cation in AN–DMF binary systems, and also Eu³⁺, La³⁺, Er³⁺ and Y³⁺ cations in AN–MeOH binary systems. This indicates that the complexes in these binary systems have lower mobility than the free solvated cations (Fig. 2).

The slope of the corresponding molar conductivity versus [L]/[M] mole ratio plots for strong complexes changes sharply at the point where the ligand to cation ratio is one, which is an evidence for formation of a relatively stable 1:1 complex. The results show, in all cases, DCH18C6 ligand forms 1:1 complexes with Eu³⁺, La³⁺, Er³⁺ and Y³⁺ cations in AN–DMF and AN–MeOH binary systems at different temperatures.

The 1:1 complexation reaction of a metal cation, Mⁿ⁺, with crown ether is represented by the following equilibrium:



The corresponding equilibrium constant, K_f, is given by:

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

where [MLⁿ⁺], [Mⁿ⁺] and [L] denote the molar concentration of the complex, metal cation and crown ether and f indicate the activity coefficient of the species indicated.

Under the highly dilute conditions which employed in these experiments, the f_{MLⁿ⁺}/f_{Mⁿ⁺}f_L is essentially unity and, therefore, the equilibrium constants obtained in this study are thermodynamic equilibrium constant.

As is seen from Tables 1 and 2, in most cases, the order of stability constant (logK_f) of (DCH18C6–La³⁺), (DCH18C6–Er³⁺) and (DCH18C6–Y³⁺) complexes in pure organic solvents is: AN > MeOH > DMF. The logK_f of these complexes in AN solvent is bigger than in pure DMF and net MEOH. In AN solvent, Gutman Donor Number (DN = 14.1) [17] is smaller than DMF (DN = 26.6) [17] and MeOH (DN = 20) [17], therefore, the solvation of the metal cations must be weaker than the other two solvents.

In Table 1, the change of logK_f with the mole fraction of DMF for DCH18C6–Er³⁺ complex in AN–DMF binary system at different temperatures shows a non-linear behavior. It is observed from this Table, the minimum of logK_f for DCH18C6–Er³⁺ complex is in χ_{AN} ~ 0.75. Thus mixing of DMF with AN induces the mutual destruction of the dipolar structures of the component liquids and releasing free dipoles. As a result, strong dipolar

Table 1 LogK_f values of DCH18C6–Eu³⁺, DCH18C6–La³⁺, DCH18C6–Er³⁺ and DCH18C6–Y³⁺ complexes in AN–DMF binary systems at different temperatures

Medium	logK _f ± SD				
	15 °C	25 °C	35 °C	45 °C	55 °C
DCH18C6–Eu³⁺					
DMF	4.12 ± 0.10	3.96 ± 0.10	4.74 ± 0.08	4.00 ± 0.01	3.82 ± 0.11
25%AN–75%DMF ^c	^a	^a	^a	^a	^a
50%AN–50%DMF ^c	^b	3.68 ± 0.13	3.83 ± 0.09	3.61 ± 0.12	^a
75%AN–25%DMF ^c	^a	^a	^a	^a	^a
AN	>6	>6	>6	>6	>6
DCH18C6–La³⁺					
DMF	3.46 ± 0.10	4.13 ± 0.11	3.54 ± 0.10	3.49 ± 0.10	3.69 ± 0.05
25%AN–75%DMF ^c	4.01 ± 0.13	4.09 ± 0.09	3.56 ± 0.13	3.65 ± 0.08	4.04 ± 0.11
50%AN–50%DMF ^c	>6	>6	>6	>6	>6
75%AN–25%DMF ^c	>6	>6	>6	>6	>6
AN	^b	^b	^b	^b	^b
DCH18C6–Er³⁺					
DMF	3.53 ± 0.11	3.89 ± 0.08	3.63 ± 0.11	3.56 ± 0.09	3.69 ± 0.10
25%AN–75%DMF ^c	3.61 ± 0.10	3.58 ± 0.11	^a	^a	^a
50%AN–50%DMF ^c	4.12 ± 0.20	3.96 ± 0.10	4.50 ± 0.01	3.74 ± 0.20	^a
75%AN–25%DMF ^c	3.37 ± 0.10	3.14 ± 0.10	3.65 ± 0.11	3.52 ± 0.09	3.70 ± 0.08
AN	>6	>6	>6	>6	>6
DCH18C6–Y³⁺					
DMF	3.90 ± 0.11	3.69 ± 0.08	3.15 ± 0.10	4.10 ± 0.20	4.08 ± 0.03
25%AN–75%DMF ^c	^b	3.52 ± 0.09	3.77 ± 0.13	3.49 ± 0.09	3.88 ± 0.02
50%AN–50%DMF ^c	3.76 ± 0.11	3.54 ± 0.07	3.55 ± 0.08	3.69 ± 0.09	^b
75%AN–25%DMF ^c	3.21 ± 0.01	3.79 ± 0.05	3.59 ± 0.08	3.61 ± 0.08	3.74 ± 0.07
AN	>6	>6	>6	>6	>6

SD Standard deviation

^a SD is high

^b The salt is not soluble

^c Composition of binary systems is expressed in mol% for each solvent system

interaction between AN and DMF molecules is expected. The observed negative values of excess adiabatic compressibility (β^E) and excess intermolecular free length (L_f^E) over the complete range of composition of AN–DMF binary mixture support the above observation. The values of excess viscosity (V^E) are negative over the whole range of mole fraction, χ of AN for AN–DMF binary systems with minimum at $\chi_{AN} \sim 0.80$ [18]. Sharma et al. [19] suggest that the molecular association between AN and DMF may be attributed to the interaction of either a fractional negative charge on the nitrogen atom of AN and the fractional positive charge on the hydrogen atom of the DMF molecule, or a fractional positive charge on the nitrogen atom of DMF and the π electron cloud of the triple bond of the AN molecule.

As is shown in Tables 2 and 3, the change logK_f with the mole fraction of MeOH for DCH18C6–Y³⁺ and DCH18C6–La³⁺ complexes in AN–MeOH binary system

is also non-linear. The minimum of logK_f for these complexes obtained in $\chi_{MeOH} \sim 0.75$ in AN–MeOH binary systems. Lee et al. [20] observed the value viscosity and density in this binary system as maximum at $\chi_{MeOH} \sim 0.7$ –0.8. Such behaviors seem to be related to the change in the structure of the solvent mixtures and solvent heterogeneity that may be a maximum at $\chi_{MeOH} \sim 0.7$ –0.8. Taheri et al. [21] also observed a non-linear behavior for the logK_f with mole fraction of MeOH in AN–MeOH binary system when studied the reaction between La³⁺, Ce³⁺ and Y³⁺ cations with some 18-membered crown ether.

The comparison of Tables 1 and 2 shows, that the selectivity order of these metal-ion complexes at 25 °C changes with the composition of AN–DMF and AN–MeOH binary systems. The selectivity order of the DCH18C6 for Eu³⁺, La³⁺, Er³⁺ and Y³⁺ cations is shown in Table 5.

Table 2 LogK_f values of DCH18C6–Eu³⁺, DCH18C6–La³⁺, DCH18C6–Er³⁺ and DCH18C6–Y³⁺ complexes in AN–MeOH binary systems at different temperatures

Medium	logK _f ± SD				
	15 °C	25 °C	35 °C	45 °C	55 °C
DCH18C6–Eu ³⁺					
MeOH	3.69 ± 0.10	3.74 ± 0.06	3.78 ± 0.09	3.54 ± 0.11	3.81 ± 0.12
25%AN–75%MeOH ^c	3.39 ± 0.09	3.55 ± 0.11	3.77 ± 0.05	3.56 ± 0.07	3.73 ± 0.10
50%AN–50%MeOH ^c	3.85 ± 0.09	3.96 ± 0.10	3.85 ± 0.11	3.71 ± 0.08	3.74 ± 0.09
75%AN–25%MeOH ^c	3.48 ± 0.11	3.46 ± 0.07	3.56 ± 0.12	3.37 ± 0.11	3.74 ± 0.08
AN	>6	>6	>6	>6	>6
DCH18C6–La ³⁺					
MeOH	4.20 ± 0.08	3.99 ± 0.07	3.89 ± 0.09	3.73 ± 0.13	^a
25%AN–75%MeOH ^c	3.03 ± 0.20	3.13 ± 0.20	3.19 ± 0.11	3.04 ± 0.13	3.83 ± 0.06
50%AN–50%MeOH ^c	3.19 ± 0.12	3.55 ± 0.08	3.89 ± 0.11	3.18 ± 0.04	4.62 ± 0.08
75%AN–25%MeOH ^c	3.17 ± 0.10	3.45 ± 0.07	3.23 ± 0.11	3.52 ± 0.09	3.93 ± 0.03
AN	^b	^b	^b	^b	^b
DCH18C6–Er ³⁺					
MeOH	4.01 ± 0.09	3.98 ± 0.08	3.81 ± 0.11	3.85 ± 0.10	3.95 ± 0.10
25%AN–75%MeOH ^c	3.61 ± 0.10	3.46 ± 0.07	3.52 ± 0.10	^a	^a
50%AN–50%MeOH ^c	3.73 ± 0.09	4.16 ± 0.10	3.69 ± 0.10	3.94 ± 0.08	4.18 ± 0.11
75%AN–25%MeOH ^c	3.45 ± 0.12	3.54 ± 0.16	3.70 ± 0.09	4.52 ± 0.09	3.70 ± 0.08
AN	>6	>6	>6	>6	>6
DCH18C6–Y ³⁺					
MeOH	^a	4.38 ± 0.12	4.14 ± 0.11	3.88 ± 0.12	4.21 ± 0.10
25%AN–75%MeOH ^c	4.07 ± 0.09	3.43 ± 0.14	3.78 ± 0.09	3.59 ± 0.04	3.97 ± 0.11
50%AN–50%MeOH ^c	4.59 ± 0.15	4.21 ± 0.11	4.26 ± 0.06	4.09 ± 0.08	4.34 ± 0.12
75%AN–25%MeOH ^c	^b	4.38 ± 0.12	4.14 ± 0.11	3.88 ± 0.12	4.21 ± 0.07
AN	>6	>6	>6	>6	>6

SD Standard deviation

^a SD is high

^b The salt is not soluble

^c Composition of binary systems is expressed in mol% for each solvent system

As it is obvious from Table 5, under identical condition, the selectivity order of DCH18C6 ligand for Eu³⁺, La³⁺, Er³⁺ and Y³⁺ cations in pure MEOH is: Y³⁺ > La³⁺ > Er³⁺ > Eu³⁺ and this is in agreement with results reported by ohyoshi et al. [22]. The Y³⁺ cation forms the most stable complex with DCH18C6 in pure MeOH solvent. These results were expected, since its ionic size of La³⁺ cation (1.17 Å) [23] is bigger than the ionic size for Y³⁺ cation (1.04 Å) [23]. Who has pointed out that as the size of lanthanides cations decreases, the charge density on cation increases, therefore, interaction with cation–ligand becomes strong. Previous studies have also shown that DB18C6 does not form any stable complex with La³⁺ cation in MEOH solution [24], that it can due to the phenyl group substituent ring of this crown ether, induces a large rigidity on the ligand, therefore, it seems that the unformational change of the ligand prevents the formation of complex in solution.

The selectivity sequence of DCH18C6 for these cations in AN–MeOH binary system (mol% MeOH = 50, 25) is Y³⁺ > Er³⁺ > Eu³⁺ > La³⁺, but in the case of other AN–MeOH (mol% MeOH = 75) is: Eu³⁺ > Er³⁺ > Y³⁺ > La³⁺. The obtained results show that the selectivity of the ligand changes with the chemical and physical properties of the constituent solvents when they are mixed with one another, which results in changing the solvation capacity of the metal cations, ligand molecules and even the resulting complexes.

The thermodynamic parameters (ΔH_c° , ΔS_c° and ΔG_c°) are summarized in Tables 3 and 4, as seen from these Tables, it seem that the changes of the thermodynamic parameters for complexation processes in AN–MeOH and AN–DMF are affected by the composition of the solvents. The interaction between unlike solvent molecules plays an important supplementary role. This leads to large deviations from the ideal behavior expected from Raoult's law of vapour

Table 3 Thermodynamic parameters for DCH18C6–Eu³⁺, DCH18C6–La³⁺, DCH18C6–Er³⁺ and DCH18C6–Y³⁺ complexes in AN–MeOH binary systems at 25 °C

Medium	$\Delta H_c^\circ \pm SD$ (KJ mol ⁻¹)	$\Delta S_c^\circ \pm SD$ (J mol ⁻¹ K ⁻¹)	$\Delta G_c^\circ \pm SD$ (KJ mol ⁻¹)
DCH18C6–Eu ³⁺			
MeOH	-6.30 ± 0.09	50.51 ± 0.28	-21.34 ± 0.03
25%AN–75%MeOH ^b	-11.32 ± 0.49	29.95 ± 1.62	-20.25 ± 0.08
50%AN–50%MeOH ^b	-11.86 ± 0.13	^a	-22.61 ± 0.27
75%AN–25%MeOH ^b	-4.02 ± 0.70	52.79 ± 0.04	-19.76 ± 0.06
DCH18C6–La ³⁺			
MeOH	-26.56 ± 1.84	46.55 ± 0.02	-12.68 ± 0.04
25%AN–75%MeOH ^b	^a	^a	-17.87 ± 0.36
50%AN–50%MeOH ^b	-6.59 ± 0.32	45.82 ± 1.06	-20.25 ± 0.05
75%AN–25%MeOH ^b	15.41 ± 0.12	58.19 ± 0.35	-19.69 ± 0.06
DCH18C6–Er ³⁺			
MeOH	-11.31 ± 0.05	38.23 ± 1.43	-22.71 ± 0.43
25%AN–75%MeOH ^b	-8.45 ± 0.10	-37.90 ± 0.27	-19.75 ± 0.06
50%AN–50%MeOH ^b	-3.82 ± 0.02	66.85 ± 0.04	-23.75 ± 0.01
DCH18C6–Y ³⁺			
MeOH	46.30 ± 0.59	-71.41 ± 1.98	-25.01 ± 0.01
25%AN–75%MeOH ^b	-20.08 ± 0.22	-1.74 ± 0.60	-19.56 ± 0.13
50%AN–50%MeOH ^b	-26.33 ± 0.10	7.75 ± 0.33	-24.02 ± 0.02
75%AN–25%MeOH ^b	-44.75 ± 0.33	7.75 ± 0.33	-25.01 ± 0.01

SD Standard deviation

^a SD is high

^b Composition of binary systems is expressed in mol% for each solvent system

Table 4 Thermodynamic parameters for DCH18C6–Eu³⁺, DCH18C6–La³⁺, DCH18C6–Er³⁺ and DCH18C6–Y³⁺ complexes in AN–DMF binary systems at 25 °C

Medium	$\Delta H_c^\circ \pm SD$ (KJ mol ⁻¹)	$\Delta S_c^\circ \pm SD$ (J mol ⁻¹ K ⁻¹)	$\Delta G_c^\circ \pm SD$ (KJ mol ⁻¹)
DCH18C6–La ³⁺			
DMF	-8.69 ± 0.04	49.91 ± 0.10	-23.57 ± 0.02
25%AN–75%DMF ^b	-30.03 ± 0.03	-22.40 ± 0.02	-23.35 ± 0.05
DCH18C6–Er ³⁺			
DMF	17.00 ± 0.12	60.67 ± 0.80	-22.21 ± 0.03
50%AN–50%DMF ^b	32.88 ± 0.20	35.13 ± 0.12	-22.61 ± 0.03
75%AN–25%DMF ^b	3.17 ± 0.01	70.73 ± 0.12	-17.92 ± 0.17
DCH18C6–Y ³⁺			
DMF	10.58 ± 0.40	^a	-1.05 ± 0.04
25%AN–75%DMF ^b	-26.45 ± 0.26	^a	-20.10 ± 0.07
50%AN–50%DMF ^b	-37.04 ± 0.10	^a	-20.20 ± 0.05
75%AN–25%DMF ^b	17.38 ± 0.02	^a	-21.64 ± 0.02

SD Standard deviation

^a SD is high

^b Composition of binary systems is expressed in mol% for each solvent system

pressure depression of binary systems. As expected, the solute is surrounded preferably by the component of the mixture which leads to the more negative Gibbs energy of solvation, $\Delta G_{\text{solv}}^\circ$.

The experimental results in Table 3 indicate that in most cases, the complexation reactions Eu³⁺, La³⁺, Er³⁺ and Y³⁺ cations with DCH18C6 ligand in AN–DMF binary systems are exothermic, and also, thermodynamic parameters

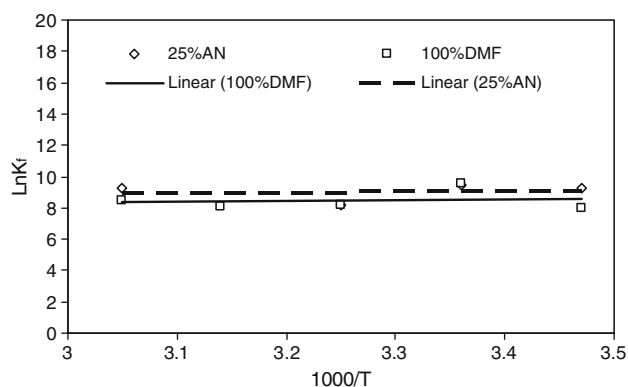


Fig. 3 Van't Hoff plots for (DCH18C6–La³⁺) complex in AN–DMF binary systems

Table 5 The selectivity order of the DCH18C6 ligand for Eu³⁺, La³⁺, Er³⁺ and Y³⁺ cation in various mediums at 25 °C

Medium	Selectivity
MeOH	Y ³⁺ > La ³⁺ > Er ³⁺ > Eu ³⁺
DMF	La ³⁺ > Eu ³⁺ > Y ³⁺ > Er ³⁺
25%AN–75%DMF	La ³⁺ > Er ³⁺ > Eu ³⁺
50%AN–50%DMF	Er ³⁺ > Eu ³⁺ > Y ³⁺
25%AN–75%DMF	Y ³⁺ > Er ³⁺
25%AN–75%MeOH	Eu ³⁺ > Er ³⁺ > Y ³⁺ > La ³⁺
50%AN–50%MeOH	Y ³⁺ > Er ³⁺ > Eu ³⁺ > La ³⁺
75%AN–25%MeOH	Y ³⁺ > Er ³⁺ > Eu ³⁺ > La ³⁺

strongly depend on the nature and concentration of the mixed solvents [25–27].

Conclusion

Since the lanthanide (III) cations have charge, small size and high coordination number [28, 29], therefore, they are capable to form complexes with crown ethers in which the complexation are accompanied by various types of interactions and hence, they show different and some contradictory behaviors in complexation with this ligand.

The selectivity of crown ethers has often been explained in terms of the size-fit concept that crown ether forms a most stable complex with the cation which has the best fit condition for the crown ether cavity. On the other hand, the results obtained in our studies suggest that the selectivity of crown ethers for the metal cations in solutions also undergoes the chemical and physical properties of each solvent such as acceptor number, donor number, polarity, relative permittivity [17] and even the structure of the solvent molecules that they change when mix with one another and, therefore, changing their solvating ability

towards the metal cations, ligand and the resulting complexes.

The results of this work also, show that the sequence of the stability of complexes of DCH18C6 with Eu³⁺, La³⁺, Er³⁺ and Y³⁺ cations changes with the composition and concentration of the mixed solvent.

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