

Thermodynamic Investigation of Complexation Process Between 18-Crown-6 with La^{3+} , Ce^{3+} , Pr^{3+} and Nd^{3+} Cations in Pure Acetonitrile and Acetonitrile-Methanol Binary Solvents at 298.15K, 308.15K and 318.15K Using Conductometric Method

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ABSTRACT: The complex formation reactions between La^{3+} , Ce^{3+} , Pr^{3+} and Nd^{3+} cations with macrocyclic ligand, 18-crown-6 ether (18C6), were studied in acetonitrile (AN)-methanol (MeOH) binary mixtures at different temperatures using conductometric method. The results show that 18C6 forms 1:1 [ML] complexes with La^{3+} , Ce^{3+} , Pr^{3+} and Nd^{3+} metal cations in solutions. The values of thermodynamic parameters and for formation of $(18\text{C}6\text{-Ln})^{3+}$ complexes were obtained from temperature dependence of the stability constants and the results show that these parameters are affected by the nature and composition of the mixed solvents.

KEYWORDS: conductometry, stability constants, thermodynamic parameters, complexation.

I. INTRODUCTION

The first report on macrocyclic compound (crown ethers) was published by C. J. Pedersen [1]. After that considerable research has been carried out on a wide range of applications of these compounds in various areas of research such as, polymer synthesis, organic synthesis and in separation of metals and many more. Crown ethers form host-guest complexes [2] with many cations, particularly with alkali, alkaline earth metal cations and also with lanthanides. Unique property of crown ethers is their ability to form stable complexes with metal cations. In the typical complex crown cavity holds the metal cation by providing full or partial inner coordination sphere due to ligating donor atoms from the crown ring. The crown ethers are of practical interest for number of reasons, they have found applications in such areas as separation of metal cations [3], phase transfer catalysis [4], selective transport of metal cations [5], recognition of isomers [6].

Lanthanides form quite stable solvates with polar solvents so that their complexes with neutral ionophoric ligands must usually be isolated from non-aqueous solutions in solvents with low to moderate donor strength, e.g. acetone or acetonitrile. The metal : ligand ratio depends upon the nature of both the Ln(III) ion and the ligand L, in

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some instances too, different experimental conditions can lead to the isolation of complexes with different stoichiometries.

There are so many techniques are available to study the complex formation between macrocyclic ligands and various metal cations in liquid phasesuch as calorimetry [7], potentiometry [8], spectrophotometry [9], polarography [10], conductometry [11], fluorescence spectroscopy [12] and NMR spectrometry [13]have been used.

II. EXPERIMENTAL

Materials and procedure

18-Crown-6 (Aldrich) was recrystallized from acetonitrile (Finar Chemicals) and dried at room temperature in vacume for 72 h. Lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) (CDH), cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) (CDH), praseodymium nitrate ($\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) (Aldrich) and neodymium nitrate ($\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) (Aldrich) were used without further purification. Acetonitrile and Methanol both from (Finar Chemicals) with the highest purity were used as solvents.

To get the formation constants of complexes, method 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, step-by-step added the crown ether solution prepared in the same solvent (2.0×10^{-3} M) by a rapid transfer to the titration cell using a micro burette. Addition of the crown solution was continued until its concentration was four times that of the metal ion. The same procedure was followed at 25 °C, 35 °C and 45 °C, and the conductivity data was used for the calculation of the formation constant of the complexes at the desired temperatures.

Apparatus

The conductance measurements were performed using a digital Metrohm (Herisau, Switzerland) conductivity apparatus, Model 856, in a water-bath thermostated at constant temperature maintained within $\pm 0.01^\circ\text{C}$. A dip type 5-ring conductivity cell having a cell constant of 0.59 cm^{-1} was used. The cell constant of the conductivity cell was determined by measuring the conductivity of aqueous potassium chloride solutions of different concentrations [14].

III. RESULT AND DISCUSSION

The changes of molar conductivity versus the ligand to cation mole ratio for the complexation of 18-crown-6 with La^{3+} , Ce^{3+} , Pr^{3+} and Nd^{3+} cations in pure acetonitrile, pure water and acetonitrile-methanol (AN-MeOH) binary systems were studied at 298.15K, 308.15K and 318.15K. Typical examples of molar conductance-mole ratio plots are shown in Figs. 1-4.

The stability constants of 18C6 crown ether complexes with La^{3+} , Ce^{3+} , Pr^{3+} and Nd^{3+} cations at each temperature were calculated from variation of molar conductance as a function of $[\text{L}]/[\text{M}]$ molar ratio using a Genplot computer program [15]. The details of calculation of the stability constants of complexes by conductometric method have been explained in reference [16].

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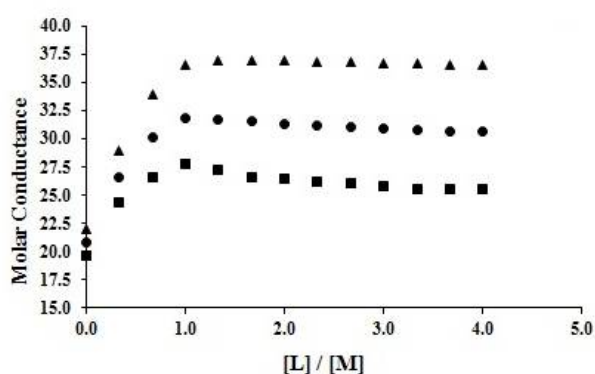


Figure 1. Molar conductance (ohm⁻¹ cm² mol⁻¹)-mole ratio plots for 18C6 -La³⁺ complex in pure AN at various temperatures : ■ = 298.15 K, ● = 308.15 K and ▲ = 318.15 K

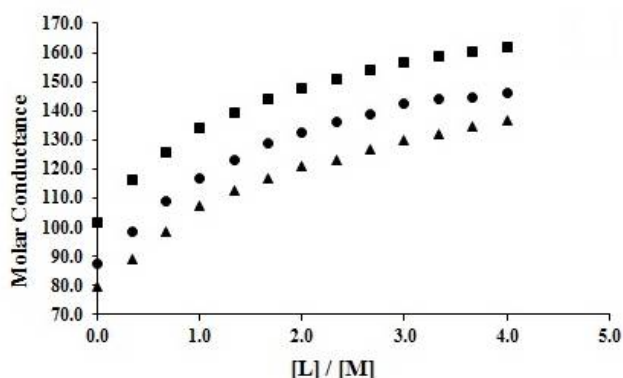


Figure 2. Molar conductance (ohm⁻¹ cm² mol⁻¹)-mole ratio plots for 18C6 -Pr³⁺ complex in AN-MeOH binary solutions (%AN = 75) at various temperatures : ■ = 298.15 K, ● = 308.15 K and ▲ = 318.15 K

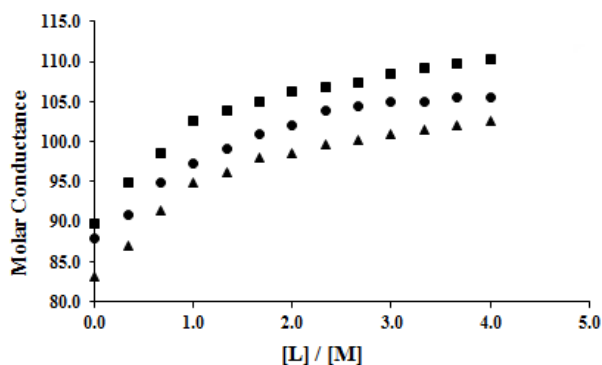


Figure 3. Molar conductance (ohm⁻¹ cm² mol⁻¹)-mole ratio plots for 18C6 -Ce³⁺ complex in AN-MeOH binary solutions (%AN = 50) at various temperatures : ■ = 298.15 K, ● = 308.15 K and ▲ = 318.15 K

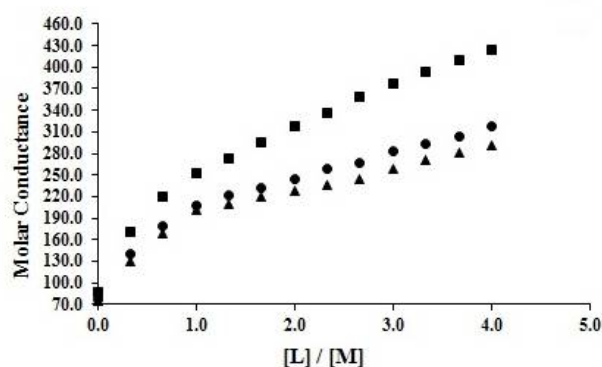


Figure 4. Molar conductance (ohm⁻¹ cm² mol⁻¹)-mole ratio plots for 18C6 -Nd³⁺ complex in AN-MeOH binary solutions (%AN = 25) at various temperatures : ■ = 298.15 K, ● = 308.15 K and ▲ = 318.15 K

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Table 1. Log K_f values of 18C6- M^{3+} complex in AN-MeOH binary mixtures at different temperatures.

Complex	Solvent Medium	Log $K_f \pm SD^a$		
		298.15 K	308.15 K	318.15 K
18C6- La^{3+}	Pure AN	4.78±0.07	4.72±0.08	4.65±0.06
	75% AN-25% MeOH	4.65±0.05	4.60±0.06	4.56±0.07
	50% AN-50% MeOH	4.43±0.03	4.40±0.04	4.37±0.04
	25% AN-75% MeOH	4.62±0.04	4.60±0.05	4.58±0.03
	Pure MeOH	b	b	b
18C6- Ce^{3+}	Pure AN	4.71±0.05	4.68±0.06	4.64±0.08
	75% AN-25% MeOH	4.60±0.04	4.57±0.04	4.54±0.06
	50% AN-50% MeOH	4.42±0.06	4.39±0.05	4.36±0.05
	25% AN-75% MeOH	4.61±0.03	4.59±0.06	4.57±0.04
	Pure MeOH	b	b	b
18C6- Pr^{3+}	Pure AN	4.59±0.06	4.49±0.07	4.38±0.07
	75% AN-25% MeOH	4.53±0.04	4.45±0.06	4.36±0.04
	50% AN-50% MeOH	4.52±0.05	4.44±0.05	4.35±0.03
	25% AN-75% MeOH	4.67±0.05	4.61±0.03	4.56±0.06
	Pure MeOH	b	b	b
18C6- Nd^{3+}	Pure AN	4.52±0.07	4.44±0.06	4.36±0.09
	75% AN-25% MeOH	4.46±0.05	4.39±0.04	4.32±0.05
	50% AN-50% MeOH	4.45±0.03	4.37±0.07	4.29±0.04
	25% AN-75% MeOH	4.64±0.04	4.58±0.04	4.52±0.06
	Pure MeOH	b	b	b

^aSD= standard deviation

From Table 2 we can see that a non-linear behavior is observed for the stability constants (log K_f) of these complexes with the composition of AN- MeOH binary system. For example, the variations of stability constant of (18C6- M^{3+}) complex with the composition of AN- MeOH binary system at different temperatures are shown in Fig. 5.

The changes of the stability constant (log K_f) for (18C6- M^{3+}) complexes versus the percentage of MeOH in AN-MeOH binary solution is not linear (Fig. 6).

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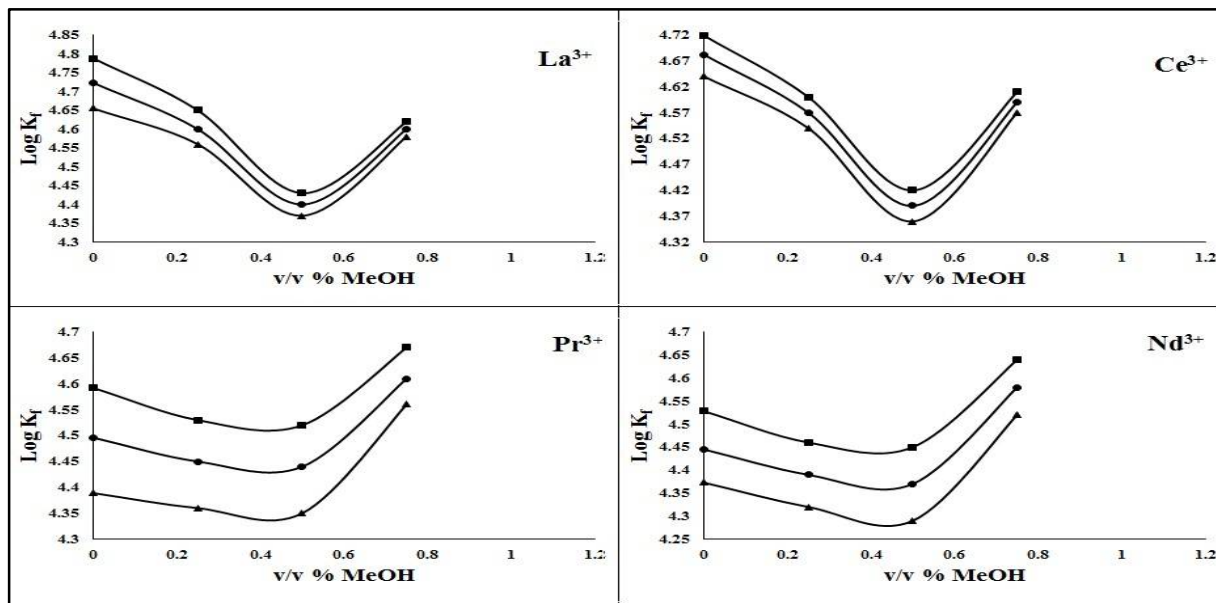


Figure 5. Change of the stability constant $\text{Log } K_f$ of (18C6-M³⁺) complex with the composition of AN-MeOH binary systems at various temperatures : ■ = 298.15 K, ● = 308.15 K and ▲ = 318.15 K

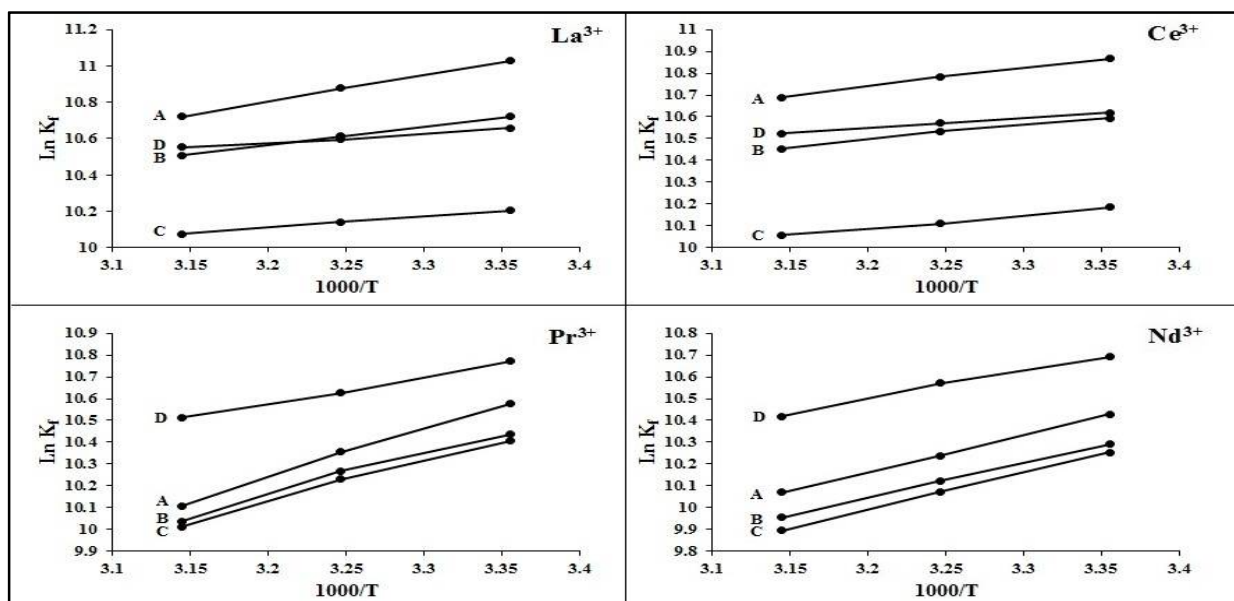


Figure 6. van't Hoff plots for the (18C6-M³⁺) complex in AN-MeOH binary systems: (A = Pure AN, B = 25% MeOH, C = 50% MeOH and D = 75% MeOH).

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Gutman Donor number indicates the solvating ability of solvent for solute so, solvents with high donor ability (high DN number), the stability constant of complex should decrease owing to competition between the ligand and the solvent molecules for the metal cation. In acetonitrile with a low Gutman Donor Number (DN = 14.1)[17] the solvation of the metal cations must be less than MeOH (DN = 19.0)[17] with a high solvating ability.

Addition of the 18C6 ligand to solutions of La^{3+} , Ce^{3+} , Pr^{3+} and Nd^{3+} cations in pure AN and all AN-MeOH binary solvent systems at different temperatures shows that the molar conductivity values increase with increasing $[\text{18C6}]/[\text{M}^{3+}]$ mole ratio which indicates that the (18C6-M^{3+}) complexes in this solvent and solvent systems have higher mobility than free solvated La^{3+} , Ce^{3+} , Pr^{3+} and Nd^{3+} cations. The slope of the corresponding molar conductivity versus $[\text{L}]/[\text{M}]$ 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, 18C6 ligand forms 1:1 complexes with La^{3+} , Ce^{3+} , Pr^{3+} and Nd^{3+} cations in pure AN, pure MeOH and AN-MeOH binary systems at different temperatures.

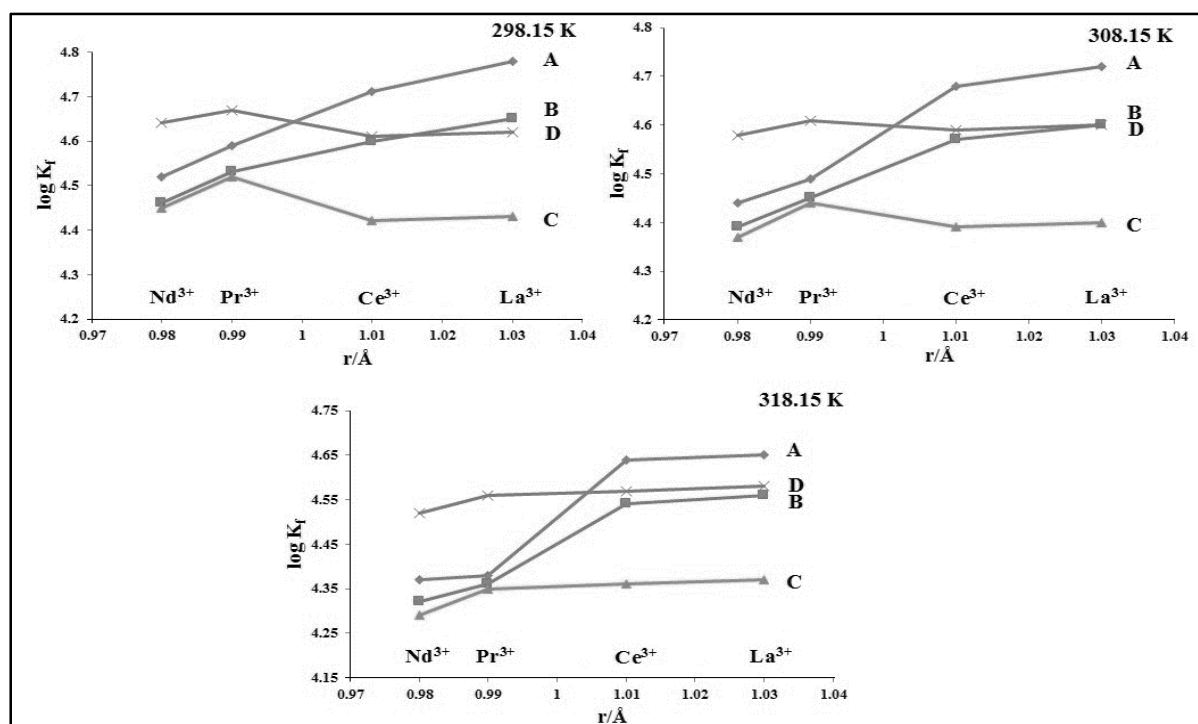


Figure 7. Variation of $\log K_f$ for 18C6-La^{3+} , 18C6-Ce^{3+} , 18C6-Pr^{3+} and 18C6-Nd^{3+} complexes versus cationic radius in AN-MeOH binary systems (A = Pure AN, B = 25% MeOH, C = 50% MeOH, D = 75% MeOH at 298.15K, 308.15K and 318.15K).

The order of stability complexes in pure AN and 75% AN at 25 °C $\text{La}^{3+} > \text{Ce}^{3+} > \text{Pr}^{3+} > \text{Nd}^{3+}$. It is interesting to note that the order of stability of the complexes formed between 18C6 and these metal cations in AN-MeOH (50 % AN

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and 25% AN) binary mixtures is $\text{Pr}^{3+} > \text{Nd}^{3+} > \text{La}^{3+} > \text{Ce}^{3+}$. This behavior for selectivity of metal cations with 18C6 is sensitive to solvent composition of the mixed solvent systems.

Solvent properties, such as donor number, dielectric constant and the isosolvation point contribute to the changes of enthalpy and entropy as a function of solvent composition.

The ionic sizes of the La^{3+} (ionic radius = 1.03 Å) [18], Ce^{3+} (ionic radius = 1.01 Å) [18], Pr^{3+} (ionic radius = 0.99 Å) [18] and Nd^{3+} (ionic radius = 0.98 Å) [18] ions are close to the size of the 18C6 cavity (2.3–3.2 Å) [19], therefore, they form stable complexes with the ligand in these media. The La^{3+} ion forms the most stable complex with 18C6 because its ionic diameter is very close to crown cavity. Plots of $\log K_f$ versus $1000/T_m$ in all cases were linear.

The variation of $\log K_f$ of (18C6- La^{3+}), (18C6- Ce^{3+}), (18C6- Pr^{3+}) and (18C6- Nd^{3+}) complexes vs. the ionic radii in pure AN and various AN-MeOH binary mixtures is shown in Figure 7. As is seen, the order of stability of complexes formed between 18C6 and these cations vary with the variation of volume of MeOH.

Table 2. Thermodynamic parameters for 18C6- M^{3+} complexes in AN-MeOH binary systems at 298.15K

Complex	Solvent Medium	$\Delta G^\circ \pm \text{SD}^a$ (kJ.mol ⁻¹)	$\Delta H^\circ \pm \text{SD}^a$ (kJ.mol ⁻¹)	$\Delta S^\circ \pm \text{SD}^a$ (J.mol ⁻¹ K ⁻¹)
18C6- La^{3+}	Pure AN	-27.78±0.07	-12.12±0.09	51.03±5
	75% AN-25% MeOH	-27.00±0.07	-8.34±0.08	61.14±6
	50% AN-50% MeOH	-25.70±0.09	-5.07±0.07	67.81±4
	25% AN-75% MeOH	-26.84±0.09	-4.06±0.07	74.93±5
	Pure MeOH	-	-	-
18C6- Ce^{3+}	Pure AN	-27.37±0.08	-7.08±0.07	66.16±6
	75% AN-25% MeOH	-26.74±0.08	-6.38±0.08	66.83±5
	50% AN-50% MeOH	-25.66±0.09	-5.03±0.07	67.75±6
	25% AN-75% MeOH	-26.74±0.07	-3.75±0.07	75.68±4
	Pure MeOH	-	-	-
18C6- Pr^{3+}	Pure AN	-26.64±0.08	-18.39±0.07	26.24±6
	75% AN-25% MeOH	-26.28±0.07	-15.64±0.08	34.34±7
	50% AN-50% MeOH	-26.21±0.07	-15.48±0.07	34.63±6
	25% AN-75% MeOH	-27.13±0.09	-10.20±0.08	55.27±5
	Pure MeOH	-	-	-

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18C6- Nd³⁺	Pure AN	-26.27±0.06	-15.22±0.09	35.62±5
	75% AN-25% MeOH	-25.92±0.07	-13.19±0.08	41.28±7
	50% AN-50% MeOH	-25.82±0.07	-14.11±0.08	37.88±5
	25% AN-75% MeOH	-26.93±0.08	-10.70±0.09	52.99±4
	Pure MeOH	-	-	-

^aSD= standard deviation

The thermodynamic parameters (ΔG_c^0 , ΔH_c^0 and ΔS_c^0) of the complex formation, calculated from the temperature dependences of the stability constants, are given in Table 2. The Gibbs energy of the complex formation Nonmonotonically varies with the composition of the binary organic solvents which indicates the inter particle interactions because of the entropy-enthalpy compensation [20]. The values of thermodynamic parameters (ΔH_c^0 and ΔS_c^0) for all of the complexes in AN– MeOH binary solutions are influenced by the solvent composition and in all cases, the complexes are enthalpy stabilized, but entropy destabilized. The results in Table 2, show that, the thermodynamic data show that in most cases, the complexation reactions between 18C6 with La³⁺, Ce³⁺, Pr³⁺ and Nd³⁺ cations are exothermic. The values of thermodynamic parameters for complexation processes in binary mixed solvents are affected by the solvation capacity of the metal cations, the macrocyclic ligand and also the metal ion complexes which depends on the structural and energetic properties of the mixed solvents.

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