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RESEARCH ARTICLE

THERMODYNAMIC STUDIES OF 18-CROWN-6 WITH La^{3+}, Ce^{3+}, Pr^{3+} AND Nd^{3+} COMPLEXES IN ACETONITRILE-WATER BINARY SOLVENT SYSTEMS AT 298.15K, 308.15K AND 318.15K BY CONDUCTOMETRIC METHOD

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ABSTRACT

The complexation reactions between 18-crown-6 (18C6) with La^{3+}, Ce^{3+}, Pr^{3+} and Nd^{3+} cations were studied in acetonitrile-water (AN-H_2O) binary solvent systems at different temperatures by the conductometric method. In all the cases, 18C6 forms a 1:1 complex with La^{3+}, Ce^{3+}, Pr^{3+} and Nd^{3+} cations. The results show that the selectivity order of 18C6 for the metal cations in AN–H_2O binary solvent systems at 298.15 K is : La^{3+}>Ce^{3+}> Pr^{3+} >Nd^{3+}. The values of stability constants of complexes, which were obtained from conductometric data, show that the stability of complexes is affected by the nature and composition of the binary mixed solvents. The corresponding thermodynamic parameters (ΔH, ΔS and ΔG) were obtained from the temperature dependence of the stability constants using van't Hoff plots. The results show that the values and also the sign of these parameters are influenced by the nature and composition of the mixed solvents.

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INTRODUCTION

After discovery of macrocyclic polyethers by Pedersen (Pedersen, 1967), many data have been published on the thermodynamic functions of complex formation of crown ethers with alkali cations, transition metals and lanthanide metals. Crownethers are capable of ion encapsulation due to their cage like structure. Crown cavity holds the metal cation by electrostatic attraction between the charged cation and dipoles created by the nonbonding electrons of donor atoms (Pedersen and Frensdorff, 1972; Izatt *et al.*, 1995). The binding ability and selectivity of crown ethers for metal ions depends on cavity size of crown ethers, metal cation radius, donor atoms type, confirmation of crown ether, the nature of solvents and etc. Solvents plays an important role in the selectivity of crown ethers for metal ions to bind (Agnihotri *et al.*, 2005; Rounaghi and Heydari, 2008). Crown ethers are used in organic synthesis (Pedersen, 1988), chemical analysis (Kolthoff, 1979), in construction of ion selective electrodes (Frensdorff, 1971), separation of metal cations (Bradshaw and Izatt, 1997). Ln^{3+} are hard acids and present strong affinity for charged ligands or neutral O- and N-donors, as literature survey shows that Ln^{+3} forms complexes in solution. Lanthanide compounds have been widely used in the last decades as luminescent chemosensors (Bunzli and Piguet, 2005), in organic synthesis, in bioorganic chemistry, for medical diagnostics and optical cell imaging (Bunzli and Piguet, 2005; Hemmilä and Laitala, 2005; New *et al.*, 2010), contrast reagents for magnetic resonance imaging (Caravan, 2009), shift reagents for NMR spectroscopy (Otting, 2008), and also as catalysis (Shibasaki and Yoshikawa, 2002). In this work we have analyzed thermodynamic parameters concerning formation of lanthanide (III) complexes with selected, O-donors (crown ethers) compounds. There are number of methods have been used to study the complex formation between macrocyclic ligands and different metal cations in solutions such as polarography (Rounaghi *et al.*, 1996), spectrophotometry (Nakamura *et al.*, 1980), potentiometry (Thaler *et al.*, 2003), NMR spectrometry (Rounaghi and Popov, 1986), calorimetry (Buschmann and Schollmeyer, 2000), conductometry (Chandra *et al.*, 2017) and fluorescence spectroscopy (Erk and Göçmen, 2000).

MATERIALS AND METHODS

Materials and procedure

18-Crown-6 (Aldrich) was recrystallized from acetonitrile (Finar Chemicals) and dried at room temperature in vacuum for 72 hrs. Lanthanum nitrate ($La(NO_3)_3 \cdot 6H_2O$) (CDH), cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$) (CDH), praseodymium nitrate

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($Pr(NO_3)_3\cdot6H_2O$) (Aldrich) and neodymium nitrate ($Nd(NO_3)_3\cdot6H_2O$) (Aldrich) were used without further purification. Acetonitrile (Finar Chemicals) with the highest purity and triple distilled water having conductivity less than 1 × 10^{-7} S/cm was used in the entire study. To determine the formation constants of complexes, procedure is as follows: a solution of metal salt (1.0 x 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 x 10^{-3} M) by a quick transfer to the titration cell using a microburette. Addition of the crown solution was continued until its concentration was four times that of the metal ion. The same procedure followed at 25°C, 35°C and 45 °C, and the conductance 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 ±0.01°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 conductance of aqueous potassium chloride solutions of different concentrations (Wu and Koch, 1991).

RESULTS AND DISCUSSION

The changes of molar conductivity versus the ligand to cation mole ratio for the complexation of 18-crown-6with La^{3+}, Ce^{3+}, Pr^{3+} and Nd^{3+} cations in acetonitrile-water(AN-H_2O) binary systems were studied at different temperatures. Typical examples of molar conductance-mole ratio plots are shown in Figs. 1-5. 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 (L)/(M) molar ratio using a Genplot computer program (Genplot, 1989). The details of calculation of the stability constants of complexes by conductometric method have been explained in reference (Chandra and Maisuria, 2013). The stability constants for 18C6 withLa^{3+}, Ce^{3+}, Pr^{3+} and Nd^{3+}metal complexes in various solvent systems are listed in Table 1. The changes in standard enthalpy (ΔH_c^0) for the complexation reactions were determined from the slopes of the van't Hoft plots assuming that ΔCp is equal to zero over the entire temperature range is investigated, and the changes in standard entropy (ΔS_c^0) were calculated from the relationship $\Delta G_{c,298.15}^0 = \Delta H_c^0 - 298.15\ \Delta S_c^0$. From the Table 2 it is clear that a non-linear behavior is observed forthe stability constants ($\log K_f$) of these complexes with the composition of AN-H_2O binary system. For example, the variations of stability constant of 18C6-M^{3+} complexes with the composition of AN-H_2O binary system at different temperatures are shown in Fig. 6. From Table 1 it is clear that in most cases, the stability constant ($\log K_f$) of (18C6-La^{3+}) complexes increases with increasing the concentration of acetonitrile in AN–H_2O binary mixture. Donor ability, the dielectric constant and even by the shape and the size of the solvent molecules influences to the solvation of the cation, ligand and the complex (Arnaud-Neu *et al*., 2003). Solvents with high donor ability (high DN number), the stability constant of complex should decrease owing to competition between ligand and solvent molecules for the metal cation. In acetonitrile with a low Gutman Donor Number (DN = 14.1) (27) the solvation of the metal cations must be less than H_2O (DN = 33) (Izutsu, 2009) with a high solvating ability. The changes of the stability constant ($\log K_f$) for (18C6-M^{3+}) complexes versus the percentage of H_2O in AN–H_2O binary solution are not linear (Fig. 6). Addition of 18C6 ligand to solutions of La^{3+}, Ce^{3+}, Pr^{3+} and Nd^{3+} cations in pureAN at different temperatures shows that the molar conductivity values increase with increasing (18C6)/(M^{3+}) mole ratio which indicates that the (18C6-M^{3+}) complexes in this solvent have higher mobility than free solvated La^{3+}, Ce^{3+}, Pr^{3+} and Nd^{3+} cations.

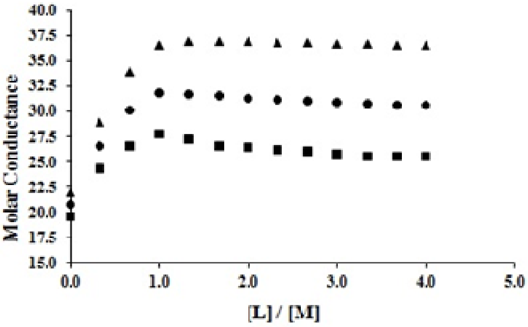

Figure 1. Molar conductance (ohm^{-1} cm^2 mol^{-1})-mole ratio plots for 18C6 -La^{3+} complex in pure AN at various temperatures :■ = 298.15 K,● = 308.15 K and ▲ = 318.15 K

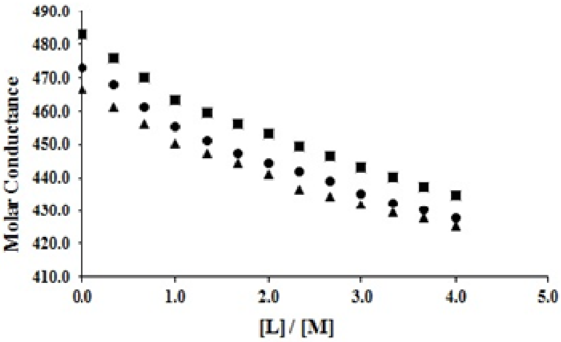

Figure 2. Molar conductance (ohm^{-1} cm^2 mol^{-1})-mole ratio plots for 18C6 -Pr^{3+} complex in AN-H_2O binary solutions (%AN = 75) at various temperatures :■ = 298.15 K,● = 308.15 K and ▲ = 318.15 K

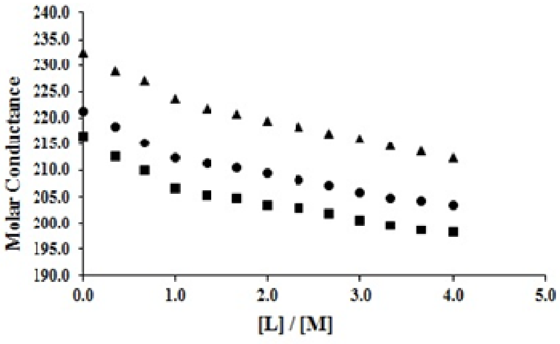

Figure 3. Molar conductance (ohm^{-1} cm^2 mol^{-1})-mole ratio plots for 18C6 -Ce^{3+} complex in AN-H_2O binary solutions (%AN = 50) at various temperatures :■ = 298.15 K,● = 308.15 K and ▲ = 318.15 K

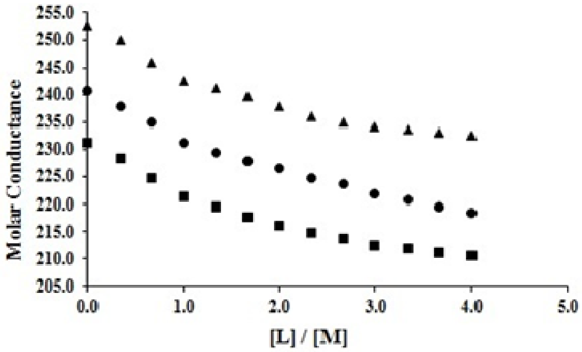

Figure 4. Molar conductance (ohm^{-1} cm^{2} mol^{-1})-mole ratio plots for 18C6 -Nd^{3+} complex in AN-H_2O binary solutions (%AN = 25) at various temperatures :■ = 298.15 K,● = 308.15 K and ▲ = 318.15 K

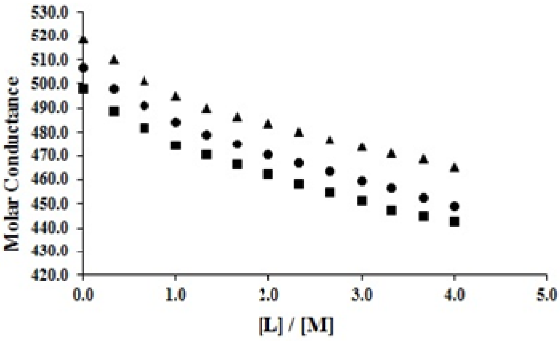

Figure 5. Molar conductance (ohm^{-1} cm^{2} mol^{-1})-mole ratio plots for 18C6 -La^{3+} complex in pureH_2O at various temperatures :■ = 298.15 K,● = 308.15 K and ▲ = 318.15 K

Table 1. Log K_f values of 18C6-M^{3+} complex in AN-H_2O binary mixtures at different temperatures

Complex	Solvent Medium	Log K_f± 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% H_2O	4.41±0.05	4.39±0.06	4.37±0.07
	50% AN-50% H_2O	4.40±0.06	4.38±0.08	4.36±0.06
	25% AN-75% H_2O	4.38±0.05	4.36±0.07	4.33±0.08
	Pure H_2O	4.39±0.06	4.41±0.06	4.43±0.07
18C6- Ce^{3+}	Pure AN	4.71±0.05	4.68±0.06	4.64±0.08
	75% AN-25% H_2O	4.38±0.08	4.37±0.07	4.36±0.06
	50% AN-50% H_2O	4.37±0.06	4.36±0.09	4.35±0.09
	25% AN-75% H_2O	4.36±0.07	4.35±0.08	4.34±0.05
	Pure H_2O	4.37±0.03	4.39±0.06	4.41±0.08
18C6- Pr^{3+}	Pure AN	4.59±0.06	4.49±0.07	4.38±0.07
	75% AN-25% H_2O	4.33±0.07	4.32±0.07	4.30±0.08
	50% AN-50% H_2O	4.32±0.06	4.31±0.08	4.29±0.06
	25% AN-75% H_2O	4.31±0.05	4.30±0.08	4.28±0.05
	Pure H_2O	4.32±0.06	4.33±0.07	4.34±0.08
18C6-Nd^{3+}	Pure AN	4.52±0.07	4.44±0.06	4.36±0.09
	75% AN-25% H_2O	4.30±0.08	4.28±0.05	4.26±0.05
	50% AN-50% H_2O	4.29±0.06	4.27±0.06	4.25±0.08
	25% AN-75% H_2O	4.27±0.08	4.26±0.08	4.24±0.06
	Pure H_2O	4.30±0.07	4.31±0.05	4.32±0.04

[a]SD= standard deviation

Table 2. Thermodynamic parameters for 18C6-M^{3+} complexes in AN-H_2O binary systems at 298.15K

Complex	Solvent Medium	ΔG°± SD[a] (kJ.mol^{-1})	ΔH° ± SD[a] (kJ.mol^{-1})	ΔS° ± 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% H_2O	-25.63±0.08	-3.90±0.08	71.42±4
	50% AN-50% H_2O	-25.56±0.09	-4.17±0.09	70.34±6
	25% AN-75% H_2O	-25.42±0.08	-4.16±0.08	69.93±7
	Pure H_2O	-25.46±0.09	4.14±0.12	97.95±6
18C6- Ce^{3+}	Pure AN	-27.37±0.08	-7.08±0.07	66.16±6
	75% AN-25% H_2O	-25.42±0.07	-1.42±0.09	79.14±7
	50% AN-50% H_2O	-25.35±0.08	-1.32±0.08	79.24±5
	25% AN-75% H_2O	-25.30±0.09	-1.31±0.09	79.06±5
	Pure H_2O	-25.40±0.07	3.05±0.11	94.08±8
18C6- Pr^{3+}	Pure AN	-26.64±0.08	-18.39±0.07	26.24±6
	75% AN-25% H_2O	-25.16±0.08	-3.13±0.09	72.51±8
	50% AN-50% H_2O	-25.08±0.07	-2.95±0.08	72.90±7
	25% AN-75% H_2O	-25.02±0.09	-2.64±0.08	73.72±6
	Pure H_2O	-25.07±0.07	2.30±0.12	90.52±5
18C6-Nd^{3+}	Pure AN	-26.27±0.06	-15.22±0.09	35.62±5
	75% AN-25% H_2O	-25.00±0.08	-4.19±0.08	68.46±8
	50% AN-50% H_2O	-24.89±0.09	-3.11±0.07	71.37±7
	25% AN-75% H_2O	-24.82±0.08	-2.87±0.09	72.28±8
	Pure H_2O	-24.97±0.07	1.59±0.1	87.77±7

[a]SD= standard deviation

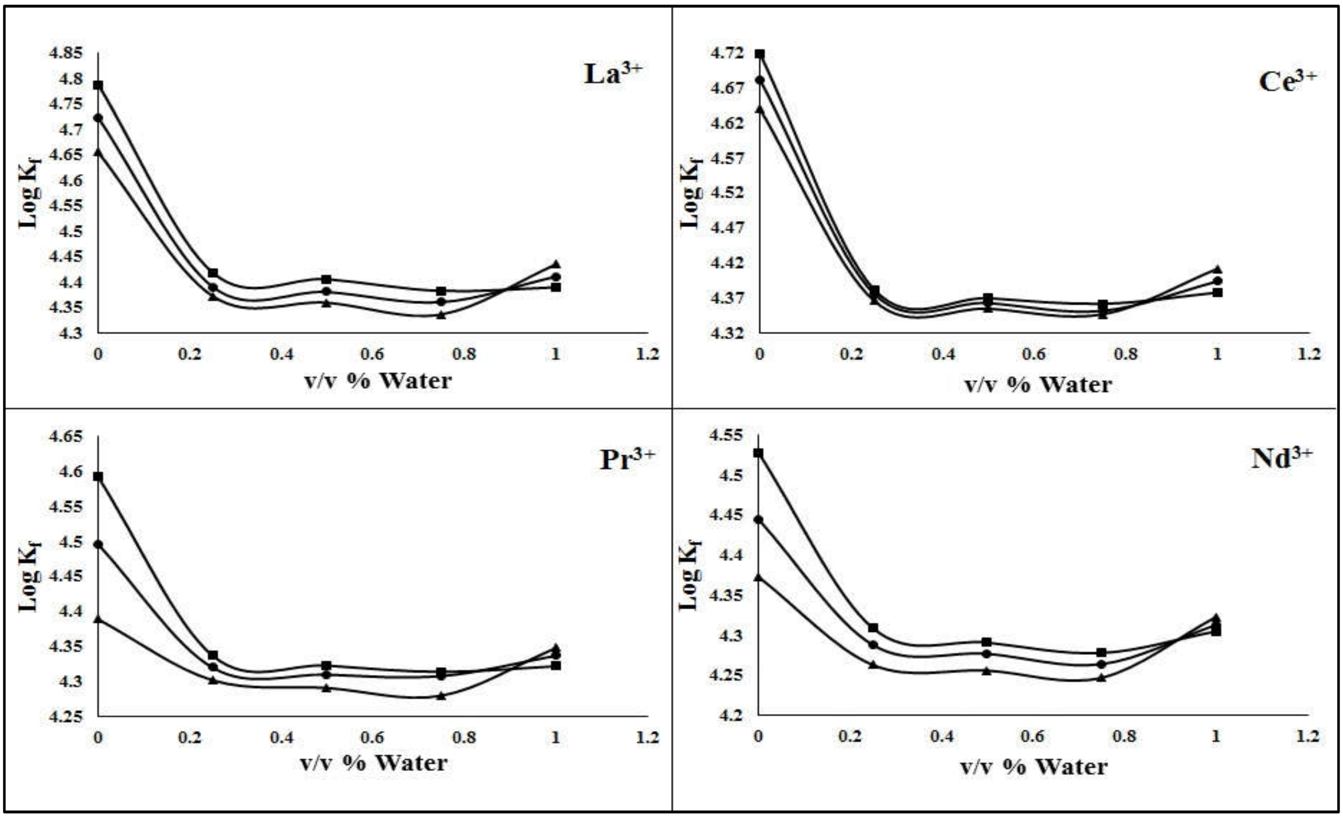

Figure 6. Change of the stability constant Log K_f of (18C6 -M^{3+}) complexes with the composition of AN-H_2O binary solvent systems at various temperatures :■ = 298.15 K,● = 308.15 K and ▲ = 318.15 K

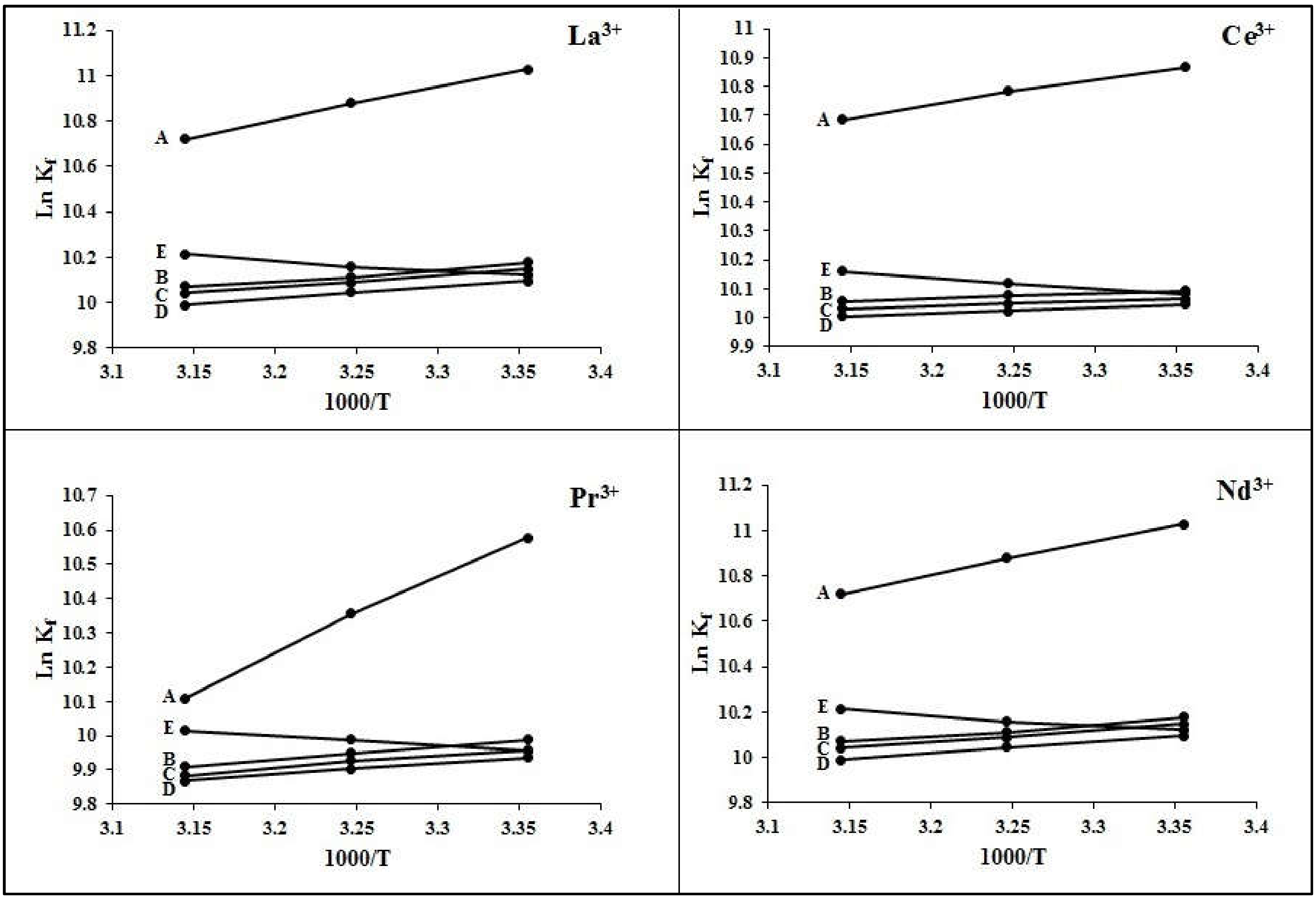

Figure 7. van'tHoff plots for the (18C6-M^{3+}) complexes in AN-H_2O binary solvent systems: (A = Pure AN, B = 25% H_2O, C = 50% H_2O, D = 75% H_2O and E = Pure H_2O)

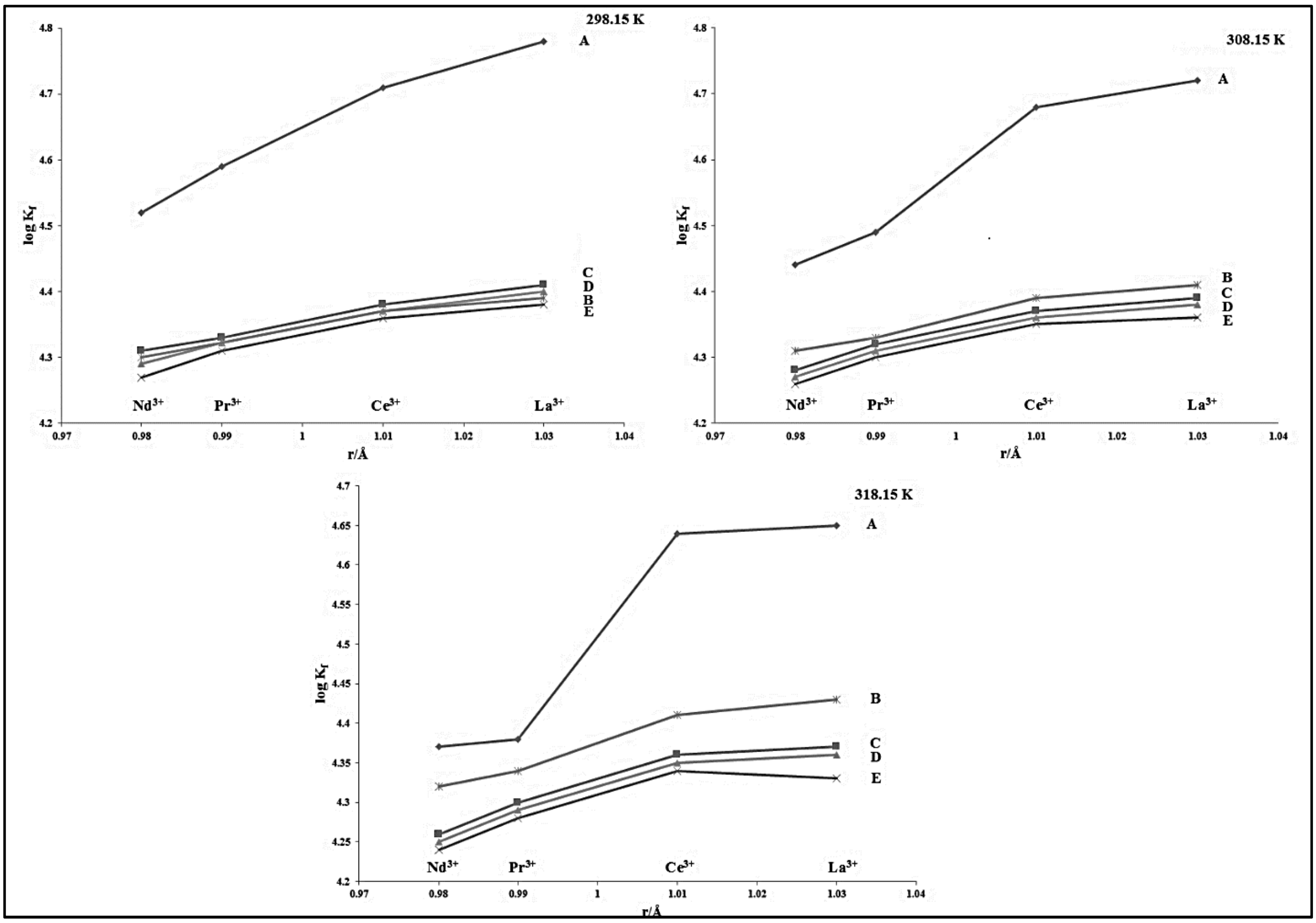

Figure 7. Variation of log K_f for 18C6-La^{3+}, 18C6-Ce^{3+}, 18C6-Pr^{3+} and 18C6-Nd^{3+} complexes versus cationic radius in ACN-H_2O binary systems (A = Pure ACN, B = Pure H_2O, C = 25% H_2O, D = 50% H_2O, E = 75% H_2O) at 298.15K, 308.15K and 318.15K

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 relativity stable 1:1 complex. On the other hand, a decrease to 1:1 mole ratio in the molar conductivity values was observed when 18C6 ligand was added to solution of La^{3+}, Ce^{3+}, Pr^{3+} and Nd^{3+} cations in all binary solvent systems and pure H_2O. This indicates that the complexes in these binary systems have lower mobility than the free solvated cations (Figs. 2-5). The results shows that in all the cases, 18C6 ligand forms 1:1 complexes with La^{3+}, Ce^{3+}, Pr^{3+} and Nd^{3+} cations in pureAN, pure H_2O and AN–H_2O binary systems at different temperatures.

The acetonitrile molecules added to water were assumed to occupy cavities in the water network structure. Douberet *et al* (Moreau and Douhéret, 1975; Moreau and Douhéret, 1974; Davis and Douhéret, 1986) inferred the presence of three structurally different regions over the AN–H_2O mixture composition range. Catalon (Catalán *et al*., 2003) also showed that the acidity, basicity and polarity for AN–H_2O binary mixture do not change linearly with the solvent composition. The selectivity order of 18C6 ligand for the metal cations in pure AN, pure H_2O and in these binary solutions is: $La^{3+} > Ce^{3+} > Pr^{3+} > Nd^{3+}$. The selectivity and stability of crown ether complexes of metal cations depend on several factors like, the cavity size of the ligand, the heteroatom character in the polyether ring, ring binding sites and the cation diameter and also the nature of the medium. The fitness of the metal cation to the cavity of a macrocyclic ligand is an important factor to explain the crown ether complexes selectivity. The ionic sizes of the La^{3+} (ionic radius = 1.03 Å) (Chandra *et al*., 2017), Ce^{3+} (ionic radius = 1.01 Å) (Chandra *et al*., 2017), Pr^{3+} (ionic radius = 0.99 Å) (Chandra *et al*., 2017) and Nd^{3+} (ionic radius = 0.98 Å) (Chandra *et al*., 2017) ions are close to the size of the 18C6 cavity (2.3–3.2 Å) (Pedersen, 1970), therefore, they form stable complexes with 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 logK_f versus 1000/Tin all cases were linear. The variation of logK_f of (18C6-La^{3+}), (18C6-Ce^{3+}), (18C6-Pr^{3+}) and (18C6-Nd^{3+}) complexes vs. the ionic radii in pure AN, pure H_2O and various AN-H_2O 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 H_2O. To understand the factors governing the complexing ability and selectivity of the crown ethers, the thermodynamic parameters must be evaluated. The thermodynamic parameters (ΔG_c^0, ΔH_c^0 and ΔS_c^0) for 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 (Frensdorff, 1971). The values of thermodynamic parameters (ΔH_c^0 and ΔS_c^0) for all of the complexes in AN–H_2O binary solvent systems are influenced by the solvent composition and in all cases, the complexes are enthalpy stabilized, but entropy destabilized. The results in Table 2 for thermodynamic data show that in most of the cases, the complexation reactions between 18C6 with La^{3+}, Ce^{3+}, Pr^{3+} and Nd^{3+} 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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