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Study of complexation process between *N-phenylaza*-15-crown-5 with yttrium cation in binary mixed solvents

Gholam Hossein Rounaghi · Behjat Deiminiat

Abstract The complexation reaction between Y^{3+} cation with *N-phenylaza*-15-crown-5(Ph-N15C5) was studied at different temperatures in acetonitrile–methanol (AN/MeOH), acetonitrile–propanol (AN/PrOH), acetonitrile–1,2 dichloroethane (AN/DCE) and acetonitrile–water (AN/H₂O) binary mixtures using the conductometric method. The results show that in all cases, the stoichiometry of the complex is 1:1 (ML). The values of formation constant of the complex which were determined using conductometric data, show that the stability of (Ph-N15C5.Y)³⁺ complex in pure solvents at 25 °C changes in the following order: PrOH > AN > MeOH and in the case of binary mixed solutions at 25 °C it follows the order: AN–DCE > AN–PrOH > AN–MeOH > AN–H₂O. The values of standard thermodynamic quantities (ΔH_c° and ΔS_c°) for formation of (Ph-N15C5.Y)³⁺ complex were obtained from temperature dependence of the formation constant using the van't Hoff plots. The results show that in most cases, the complex is entropy and enthalpy stabilized and these parameters are influenced by the nature and composition of the mixed solvents. In most cases, a non-linear behavior was observed for variation of log K_f of the complex versus the composition of the binary mixed solvents. In all cases, an enthalpy–entropy compensation effect was observed for formation of (Ph-N15C5.Y)³⁺ complex in the binary mixed solvents.

Keywords *N*-phenylaza-15-crown-5 · Y³⁺cation · Acetonitrile–methanol · Acetonitrile propanol · Acetonitril–1,2-dichloroethane · Acetonitrile–water binary mixtures · Conductometry · Enthalpy–entropy compensation

G. H. Rounaghi (✉) · B. Deiminiat
Department of Chemistry, Faculty of Sciences,
Ferdowsi University of Mashhad, Mashhad, Iran
e-mail: ghrounaghi@yahoo.com

Introduction

Crown ethers which first synthesized in 1967 by Pedersen [1], are macrocyclic polyethers which are able to form stable and selective complexes with various metal cations [2–4]. Complexes formed by crown ethers, can be utilized as solvent extraction agents [5], construction of ion selective electrodes [6, 7], selective separation [8], selective ion-transport [9] and liquid chromatography [10]. The solvation of crown ether, metal cation, the resulting complex and even the counter ion are of great importance during the complex formation of these macrocyclic ligands with metal cations in solutions. Therefore, study the influence of the nature and composition of solvent systems upon crown ether complexation is important. Contrary to the wide range of information about the complex formation between crown compounds and metal cations in various pure solvents [11–13], the data in mixed non-aqueous solvents are spares [14–16].

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 [17–19].

In this paper, the results of thermodynamic study for complexation reaction between Ph-N15C5 (Scheme 1) with Y^{3+}cation in pure organic solvents: acetonitrile (AN), methanol (MeOH) and propanol (PrOH) and also in acetonitrile–methanol (AN/MeOH), acetonitrile–propanol (AN/PrOH), acetonitrile–1,2 dichloroethane (AN/DCE) and acetonitrile–water (AN/H₂O) binary mixtures at different temperatures using conductometric method are reported.

Experimental

Ph-N15C5 (Merck) and yttrium nitrate (Merck) were used without further purification. Acetonitrile, methanol,
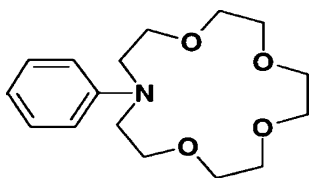
Scheme 1 Structure of *N-phenylaza-15-crown-5* (Ph-N15C5)

propanol and 1,2 dichloroethane all from Merck company and triply distilled water were used as solvents.

The conductance measurements were performed on a Genway model 4510 conductometer in a thermostated water-bath with a constant temperature maintained within ±0.03 °C. A conductometric cell with a cell constant of 0.98 Cm^{-1} was used throughout the studies.

The experimental procedure to obtain the formation constant of the complex 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 a step-by-step increase of the crown ether solution prepared in the same solvent (2.0×10^{-3} M) was carried out by a rapid transfer to the titration cell using a microburette and the conductance of the solution was measured after each step at the desired temperature.

Result

The changes of molar conductivity (Λ_m) versus the ligand to cation mole ratio $[L]_t/[M]_t$ for the complexation of Ph-N15C5 with Y^{3+} cation in acetonitrile–methanol (AN/MeOH), acetonitrile–propanol (AN/PrOH), acetonitrile–1,2 dichloroethane (AN/DCE) and acetonitrile–water (AN/H₂O) binary mixtures were studied at different temperatures. Two typical series of molar conductance values as a function of $[L]_t/[M]_t$ for (Ph-N15C5.Y)$^{3+}$ complex in AN–DCE binary system (mol% AN = 50) and in pure AN are shown in Figs. 1 and 2, respectively.

The stability constant of (Ph-N15C5.Y)$^{3+}$ complex at each temperature was obtained from variation of molar conductance as a function of $[L]_t/[M]_t$ molar ratio plots using a GENPLOT computer program [20]. The details of calculation of the stability constants of complexes by conductometric method have been described in reference [21]. The values of the stability constant (log K_f) for the (Ph-N15C5.Y)$^{3+}$complex in various solvent systems are listed in Table 1.

Plots of LnK$_f$ versus 1/T in all cases were linear and a typical example of these plots is shown in Fig. 3. The changes in standard enthalpy (ΔH_c°) for complexation reaction were determined 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 of standard
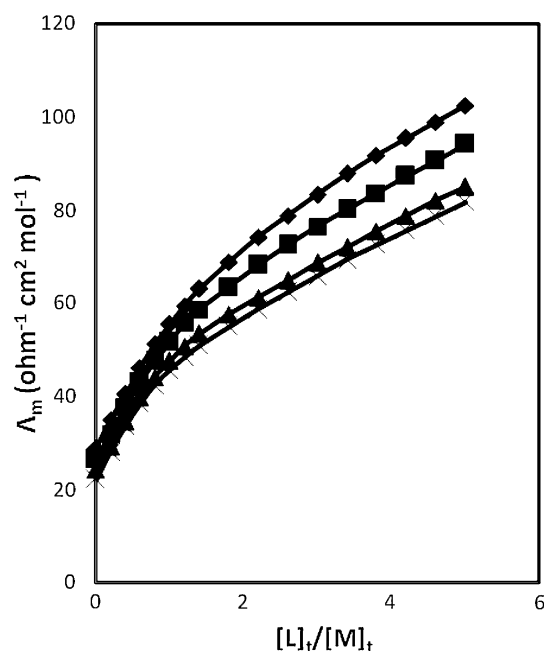

Fig. 1 Molar conductance–mole ratio plots for (Ph-N15C5.Y)$^{3+}$ complex in AN–DCE binary system (mol% AN = 50) at different temperatures: *diamond* 15 °C, *square* 25 °C, *triangle* 35 °C, *times* 45 °C
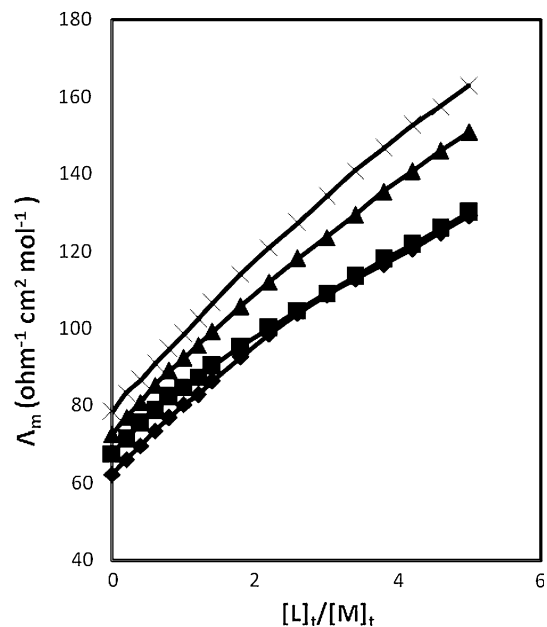

Fig. 2 Molar conductance–mole ratio plots for (Ph-N15C5.Y)$^{3+}$ complex in pure AN at different temperatures: *diamond* 15 °C, *square* 25 °C, *triangle* 35 °C, *times* 45 °C

entropy (ΔS_c°) were calculated from the relationship: $\Delta G_{c, 298.15}^\circ = \Delta H_c^\circ - 298.15 \Delta S_c^\circ$. The results are summarized in Table 2. The changes of log K_f of (Ph-N15C5.Y)$^{3+}$complex versus the mole fraction of AN in AN–DCE and AN–PrOH binary systems at different temperatures are shown

Table 1 Log K_f values of (Ph-N15C5.Y)$^{3+}$ complex in AN–MeOH, AN–PrOH, AN–DCE, AN–H$_2$O binary systems at different temperatures

mol% AN	log $K_f \pm$ SD[a]			
	15 °C	25 °C	35 °C	45 °C
AN–MeOH[b]				
100	3.08 ± 0.03	2.96 ± 0.05	2.80 ± 0.03	2.80 ± 0.02
75	2.69 ± 0.04	2.76 ± 0.09	2.78 ± 0.10	2.79 ± 0.10
50	2.78 ± 0.08	2.74 ± 0.10	2.74 ± 0.10	2.71 ± 0.13
25	2.97 ± 0.02	2.87 ± 0.06	2.78 ± 0.11	2.71 ± 0.12
0	2.85 ± 0.06	2.82 ± 0.07	2.78 ± 0.08	2.73 ± 0.03
AN–PrOH[b]				
100	3.08 ± 0.03	2.96 ± 0.05	2.80 ± 0.03	2.80 ± 0.02
75	2.84 ± 0.07	2.83 ± 0.07	2.80 ± 0.09	2.79 ± 0.08
50	2.84 ± 0.07	2.83 ± 0.07	2.81 ± 0.07	2.70 ± 0.06
25	3.03 ± 0.03	3.04 ± 0.05	3.05 ± 0.05	3.11 ± 0.03
0	3.22 ± 0.08	3.15 ± 0.03	3.12 ± 0.08	3.11 ± 0.08
AN–DCE[b]				
100	3.08 ± 0.03	2.96 ± 0.05	2.80 ± 0.03	2.80 ± 0.02
75	3.08 ± 0.04	3.17 ± 0.04	3.20 ± 0.02	3.20 ± 0.06
50	3.51 ± 0.03	3.55 ± 0.05	3.55 ± 0.07	3.56 ± 0.07
25	3.93 ± 0.07	3.94 ± 0.08	3.98 ± 0.09	3.98 ± 0.09
AN–H$_2$O[b]				
100	3.08 ± 0.03	2.96 ± 0.05	2.80 ± 0.03	2.80 ± 0.02
75	2.76 ± 0.10	2.74 ± 0.12	2.71 ± 0.12	2.69 ± 0.13
50	2.77 ± 0.10	2.69 ± 0.13	2.70 ± 0.13	2.69 ± 0.13
25	2.79 ± 0.08	2.73 ± 0.11	2.69 ± 0.13	2.69 ± 0.13

[a] Standard deviation

[b] The composition of binary mixtures is expressed in mol% for each solvent system

in Figs. 4 and 5. Plots of the enthalpy versus entropy values for (Ph-N15C5.Y)$^{3+}$ complex in binary mixed solvents are shown in Fig. 6.

Discussion

As is seen from Figs. 1 and 2, addition of Ph-N15C5 to yttrium(III) cation solution in pure AN and AN–DCE binary system (mol% AN = 50) at different temperatures shows an increase in molar conductivity, which indicates that the (Ph-N15C5.Y)$^{3+}$ complex is more mobile than free solvated Y^{3+} cation. Similar behavior was observed in all other solvent systems. As is evident in Fig. 1, the slope of the corresponding molar conductivity versus ligand/cation mole ratio plots changes at the point where the ligand to cation mole ratio is about one, which is an evidence for formation of a 1:1 [M:L] complex in solution. It is obvious from Fig. 2 that as the temperature increases, the curvature of the plots of (Ph-N15C5.Y)$^{3+}$ complex decreases, which
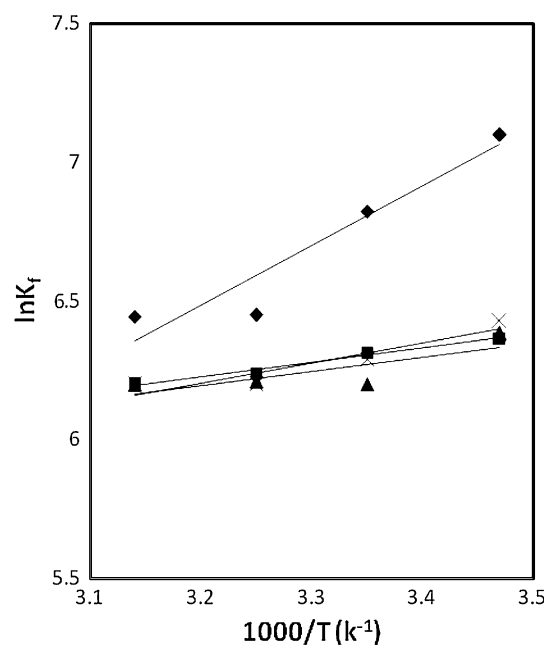
Fig. 3 van't Hoff plots for (Ph-N15C5.Y)$^{3+}$ complex in AN–H$_2$O binary systems. mol% AN: *diamond* 100.0, *triangle* 75.0, *times* 50.0, *square* 25.0

is an evidence for formation of a weaker complex at high temperatures. Therefore, the complexation process between Ph-N15C5 and Y^{3+} cation in pure AN is exothermic. The data in Table 1 show that as the concentration of 1,2 dichloroethane is increased in AN–DCE binary mixtures, the stability of (Ph-N15C5.Y)$^{3+}$ complex increases. In a weak solvating solvent such as DCE with a low donor number (DN = 0.0) the solvation of the metal cation and possibly of the ligand should be weaker than AN with a medium donor ability (DN = 14.1), therefore, the (Ph-N15C5.Y)$^{3+}$ complex becomes more stabilized as the concentration of DCE increases in AN–DCE binary solutions. As is shown in Table 1, the formation constant of (Ph-N15C5.Y)$^{3+}$ complex increases with increasing the temperature in AN–DCE binary solutions and, therefore, there is an endothermic reaction between Y^{3+} cation with Ph-N15C5 in these binary mixed solvents. But in most of the solvent systems, the formation constant of the complex decreases with increasing the temperature, which is an evidence for an exothermic complexation reaction in solutions.

Comparison of the data given in Table 1 reveals that, the stability of (Ph-N15C5.Y)$^{3+}$ complex in various pure non-aqueous solvents at 25 °C decreases in the order: PrOH > AN > MeOH. This behavior reflects the much stronger cation solvation by MeOH, compared with the other two organic solvents. Methanol with a high donor ability (DN = 20.0) relative to propanol (DN = 18.0) and acetonitrile (DN = 14.1), can solvate the Y^{3+} cation

Table 2 Thermodynamic parameters for (Ph-N15C5.Y)$^{3+}$ complex in AN–MeOH, AN–PrOH, AN–DCE, AN–H$_2$O binary mixtures

mol% AN	$\Delta G_c^\circ \pm SD^a$ 25 °C (kJ/mol)	$\Delta H_c^\circ \pm SD^a$ (kJ/mol)	$\Delta S_c^\circ \pm SD^a$ (J/mol K)
AN–MeOH[b]			
100	−16.90 ± 0.13	−17.90 ± 4.08	c
75	−15.76 ± 0.38	5.41 ± 1.90	70.58 ± 6.28
50	−15.67 ± 0.45	−3.76 ± 0.63	40.09 ± 2.08
25	−16.36 ± 0.20	−15.04 ± 0.93	c
0	−16.11 ± 0.26	−6.90 ± 0.99	30.69 ± 3.27
AN–PrOH[b]			
100	−16.90 ± 0.13	−17.90 ± 4.08	c
75	−16.14 ± 0.26	−3.27 ± 0.63	43.10 ± 2.09
50	−16.16 ± 0.26	−7.42 ± 2.85	29.03 ± 9.42
25	−17.35 ± 0.11	4.26 ± 1.39	72.55 ± 4.58
0	−17.97 ± 0.05	−6.24 ± 1.74	39.74 ± 5.74
AN–DCE[b]			
100	−16.90 ± 0.13	−17.90 ± 4.08	c
75	−18.07 ± 0.07	7.31 ± 2.19	84.70 ± 7.23
50	−20.25 ± 0.03	c	77.25 ± 3.73
25	−22.48 ± 0.02	2.94 ± 0.98	85.47 ± 3.23
AN–H$_2$O[b]			
100	−16.90 ± 0.13	−17.90 ± 4.08	c
75	−15.64 ± 0.54	−4.18 ± 0.36	38.38 ± 1.18
50	−15.37 ± 0.65	c	38.26 ± 7.44
25	−15.59 ± 0.50	−5.75 ± 1.53	33.2 ± 5.06

[a] Standard deviation

[b] The composition of binary mixtures is expressed in mol% for each solvent system

[c] With high uncertainty

Fig. 4 Changes of stability constant of (Ph-N15C5.Y)$^{3+}$ complex with the composition of the AN–DCE binary mixture at different temperatures: *diamond* 15 °C, *square* 25 °C, *triangle* 35 °C, *times* 45 °C

Fig. 5 Changes of stability constant of (Ph-N15C5.Y)$^{3+}$ complex with the composition of the AN–PrOH binary mixture at different temperatures: *diamond* 15 °C, *square* 25 °C, *triangle* 35 °C, *times* 45 °C

strongly and compete with the ligand for Y^{3+} cation. In spite of medium donor ability of acetonitrile, the stability of the complex in this solvent is lower than propanol system. It seems that the other chemical and physical properties of these organic solvents such as acceptor ability, dielectric constant, dipole moment and even the size and shape of the solvent molecules may be effective in the complexation process between the Ph-N15C5 and Y^{3+} cation in these solvent systems.

The formation constant of (Ph-N15C5.Y)$^{3+}$ complex in the binary mixed solvent solutions at 25 °C varies in the order: AN–DCE > AN–PrOH > AN–MeOH > AN–H$_2$O. Since the donor number and also the dielectric constant of water are higher than methanol, propanol and 1,2 dichloroethane, therefore, the complex formation is weakened in AN–H$_2$O binary solutions compared to the other binary mixed solvent systems. It is known that the donor ability and dielectric constant of the solvent play an important role in different complexation reactions. The stability 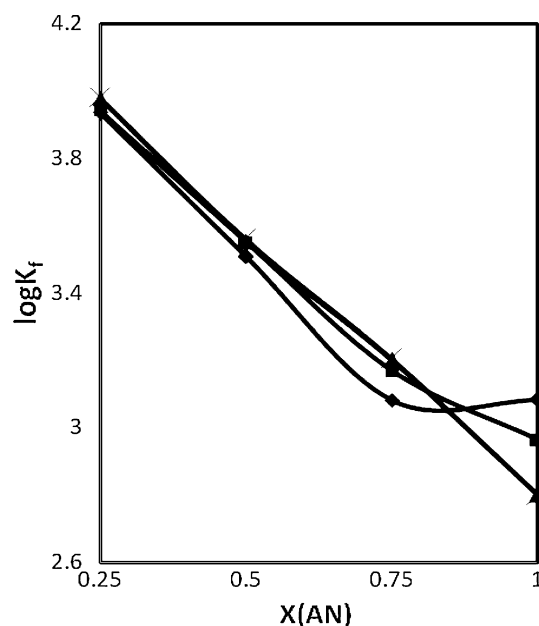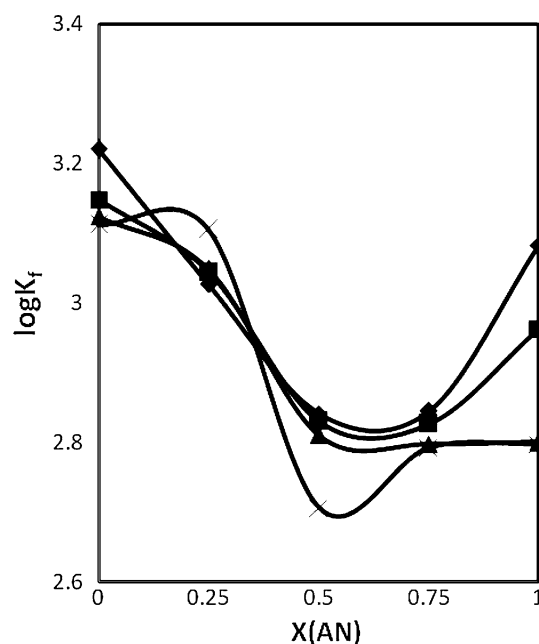constants (logK$_f$) of (Ph-N15C5.Y)$^{3+}$ complex and some of the complexes of alkali metal cations with Ph-N15C5 ligand are given in Table 3. As can be seen from this Table, the Y^{3+} cation forms a more stable complex with Ph-N15C5 in pure MeOH than Na$^+$, K$^+$ and Cs$^+$ cations. Although the ionic radius size of Y^{3+} cation (0.93 Å) is smaller than the size
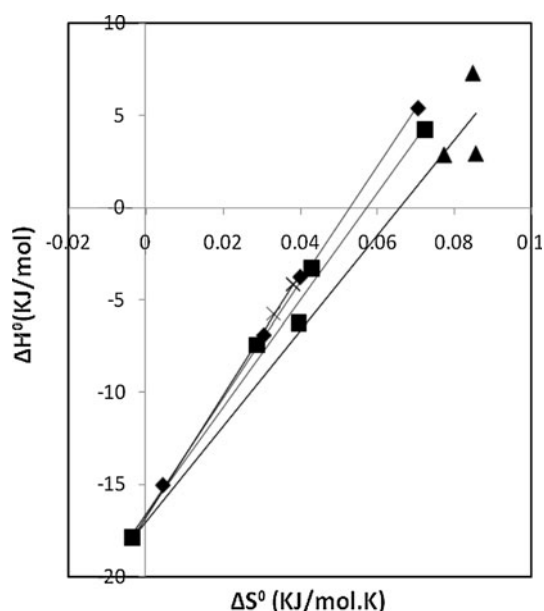
Fig. 6 Plots of the enthalpy versus entropy values for (Ph–N15C5.Y)$^{3+}$ complex in binary mixed solvents: *diamond* AN–MeOH, *square* AN–PrOH, *triangle* AN–DCE, *times* AN–H$_2$O

of the Ph-N15C5 cavity (1.7–2.7 Å) [22], but since the Y^{3+} cation is a softer acid than alkali metal cations, therefore, the interaction of this metal cation with the nitrogen atom of Ph-N15C5 ligand is stronger than the alkali metal cations in this organic solvent. As illustrated in Fig. 4, the changes of log K$_f$ of (Ph-N15C5.Y)$^{3+}$ complex versus the composition of AN–DCE binary system at most temperatures are linear. But in the case of 15 °C a non-linear relationship is observed. The different behavior which is observed at this temperature may be related to the changes occurring in the structure of the solvent mixtures with changing the temperature. The variation of logK$_f$ of (Ph-N15C5.Y)$^{3+}$ complex versus the composition of AN–PrOH binary system at various temperatures is not linear (Fig. 5). Similar behavior was observed in the other binary solutions. This behavior may be due to the interactions between solvent molecules in their binary mixtures which result in changing the structure of the mixed solvents and, therefore, changing the solvation of the cation, ligand and the resulting complex in solutions. In addition, the heteroselective solvation of these species in these mixed solvents may be another reason for this kind of behavior. The effect of properties of AN–H$_2$O and other organic-water binary mixtures on the solvation enthalpy of 15C5 and some of the other crown ethers has been studied by Jozwiak [23] and it has been shown that the crown ethers are preferentially solvated by organic solvents in these binary mixtures and it has been discussed that in these mixed solvents, the energetic effect of the preferential solvation depends quantitatively on the structural and energetic properties of the mixtures.

The values of standard thermodynamic quantities (ΔH_c° and ΔS_c°) for complex formation of (Ph–N15C5.Y)$^{3+}$ are given in Table 2. The experimental values of ΔH_c° and ΔS_c° show that with the exception of AN–DCE binary systems, in most cases, the complex is entropy and enthalpy stabilized, therefore, the enthalpy and entropy of complexation reaction are the principal driving forces for formation of this complex in most solvent systems. As is obvious from Table 2, the values of thermodynamic parameters are influenced by the nature and composition of the mixed solvents, but they do not vary monotonically with the solvent composition. This behavior may be due to the interactions between the constituent solvent molecules in their binary mixtures which result in changing in some of the chemical and physical properties of each of the solvents, and therefore, changing their solvating ability towards the dissolved species in solutions.

In addition, since there are many factors, which contribute to enthalpies and entropies of complexation reaction, therefore, we should not expect a monotonic relationship between these parameters and the composition of the binary mixed solvents.

The thermodynamic results show enthalpy–entropy compensation effects found in the binary mixed solvents, wherein as the complexation process becomes more enthalpically favorable, there is a greater loss of entropy. As is shown in Fig. 6, a remarkably linear relationship between ΔH_c° and ΔS_c° for complexation reaction between Ph-N15C5 with Y^{3+} cation is observed. The graph of enthalpy versus entropy values for complex formation of (Ph-N15C5.Y)$^{3+}$ in AN–H$_2$O binary systems produces a highly linear trend and can be expressed by the following equation:

$$\Delta H_c^\circ = 329.81(2.00)\Delta S_c^\circ - 16.76(0.06).$$

The slope of the correlation has unit of temperature and is called the compensation temperature (T$_C$). At this temperature, any variation in the standard enthalpy is balanced by a compensation variation in the standard entropy, such that the total free energy (ΔG_c°) of the complexation process remains constant.

There are several tests that can be applied to evaluate whether there is possible chemical significance to an apparent enthalpy–entropy correlation [24, 25]. When the

Table 3 Log K$_f$ values for complexation reaction of some cations with Ph-N15C5 in pure MeOH at 25 °C

cation	Na^{+b}	K^{+b}	Cs^{+b}	Y^{3+c}
log K$_f$ ± SD^a	2.49 ± 0.03	1.83 ± 0.03	1.37 ± 0.03	2.82 ± 0.07

^{a} Standard deviation

^{b} Ref. [26]

^{c} This work

Table 4 Values of slope, intercept and R^2 for enthalpy–entropy plots in AN–MeOH, AN–PrOH, AN–DCE, AN–H$_2$O binary mixtures

Medium	Slope	Intercept	R^2
AN–MeOH	314.30 ± 3.89	-16.59 ± 0.15	0.999
AN–PrOH	290.63 ± 17.49	-16.63 ± 0.76	0.989
AN–DCE	259.20 ± 30.65	-17.01 ± 2.19	0.972
AN–H$_2$O	329.81 ± 2.00	-16.76 ± 0.06	0.999

mixtures of acetonitrile–water were used as the solvent, the average experimental temperature for complexation reaction between Ph-N15C5 with Y^{3+} cation was significantly different from the observed compensation temperature (303.15 K versus 329.81 ± 2.00 K). According to this test, we can conclude that the observed correlation between enthalpy and entropy values in AN–H$_2$O binary systems has true chemical significance. Similar behavior was observed in AN–DCE binary solvent systems. As is obvious from Table 4, the average experimental temperature for complexation reaction between Ph-N15C5 with Y^{3+} cation in AN–MeOH binary systems is close to the observed compensation temperature (303.15 K versus 314.30 ± 3.89 K). This result may suggest that the apparent enthalpy–entropy correlation is an artifact from the initial van't Hoff study and the actual values of ΔH_c° and ΔS_c° for the complexation process in AN–MeOH binary systems cannot be determined accurately. Similar behavior was observed in AN–PrOH binary solvent solutions. However, the different trends observed for the formation of $(Ph\text{-}N15C5.Y)^{3+}$ complex in the binary mixed solvent systems, suggest that the solvation plays a key factor in the complexation process. The observed ΔH_c° values in AN–H$_2$O binary systems are primarily assigned to the energetic balance of the hydrogen bonds released and formed during the reaction, while the observed ΔS_c° values are due to the rearrangement of solvent molecules. The enthalpic and entropic factors in solvent hydrogen bond rearrangements are inversely related, which may result in the observed compensation behavior. In this view, enthalpically favorable hydrogen bond formation leads to a loss of entropy. The complexation reaction between Ph-N15C5 and Y^{3+} cation, involves complete desolvation of the cation and crown ether. Upon desolvation, the released solvent molecules in AN–H$_2$O binary systems can subsequently form more hydrogen bonds with each other and the bulk solution, resulting in favorable ΔH_c° values. The formation of this hydrogen bonding network, results in a decrease in ΔS_c° as the solvent becomes more ordered.

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