

Solvent influence upon complexation of *N*-phenylaza-15-crown-5 with UO_2^{2+} cation in binary mixed non-aqueous solvents

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Abstract The complexation reaction of *N*-phenylaza-15-crown-5 (PhA15C5) with UO_2^{2+} cation was studied in acetonitrile–methanol (AN–MeOH), acetonitrile–butanol (AN–BuOH), acetonitrile–dimethylformamide (AN–DMF) and methanol–propylencarbonate (MeOH–PC) binary solutions, at different temperatures by conductometry method. The conductance data show that the stoichiometry of the complex formed between PhA15C5 with UO_2^{2+} cation in most cases is 1:1 [M:L], but in some solvent systems a 1:2 [M:L₂] complex is formed in solutions. The results revealed that, the stability constant of $(\text{PhA15C5}\cdot\text{UO}_2)^{2+}$ complex in the binary mixed solvents varies in the order: AN–BuOH>AN–MeOH>AN–DMF. In the case of the pure organic solvents, the sequence of the stability of the complex changes as: AN>PC>BuOH>DMF. A non-linear relationship was observed for changes of $\log K_f$ of $(\text{PhA15C5}\cdot\text{UO}_2)^{2+}$ complex versus the composition of the binary mixed solvents. The corresponding standard thermodynamic parameters (ΔH_c° , ΔS_c°) were obtained from temperature dependence of the stability constant. The results show that the values and also the sign of these parameters are influenced by the nature and composition of the mixed solvents.

Keywords *N*-phenylaza-15-crown-5 · UO_2^{2+} cation · Mixed non-aqueous solvents · Conductometry

Introduction

The study of complexation reactions of the uranyl cation with crown ethers in nonaqueous matrices is of certain scientific interest and can be useful to the wide circle of specialists in area of inorganic, coordination, extraction and analytical chemistry.

A key chemical process in the nuclear industry is the extraction and purification of uranium in the initial production of fuel for nuclear reactors and in the reprocessing of spent nuclear fuel. Uranyl can easily form complexes with various types of ligands. Several studies have been carried out to enhance the selectivity in the separation of lanthanides and actinides elements in the extraction systems based on the size-fitting effect of the crown ethers [1–3].

Aza-crown ethers are suitable complexing agents for transition and heavy metal cations because when one or two oxygen donors in crown ethers are replaced by nitrogen atoms, the stability constants of complexes of the resulting aza-crown ethers with alkali and alkaline earth metal cations become smaller than those of the corresponding crown ethers. In contrast, the complexation abilities with transition metal cations and also heavy metal cations increase markedly to the same level as the corresponding acyclic amines [4].

The binding ability and selectivity of crown ethers to metal cations depend on several factors: such as the size of the crown ether cavity, metal ion radius, type of donor atoms, conformation of the crown ether, the nature of the solvent and etc. Solvent plays a crucial role in the binding selectivity of the crown ethers for the metal cations [5, 6].

The influence of the solvent on a variety of chemical phenomena, including solubility, phase transfer, chemical equilibria thermodynamic and kinetics are among the most

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important issues in molecular recognition processes [7, 8]. Thus, the solvent characteristics, which include properties such as the level of structure, polarity, hydrogen bond donor/acceptor ability, polarizability, acidity/basicity, and hydrophobicity/hydrophilicity and other empirical parameters, mainly affect the interaction strength between the solvent molecules and the dissolved species [9, 10]. As a result, the stability and selectivity of crown ether complex formation with metal cations are influenced by the interaction of the solvent molecules with the cation, crown ether and the resulting complex as well. Therefore, if the solvent is changed, a significant effect on the stability constant of the complex is observed especially where the cation and the ligand are strongly solvated by the solvent molecules [11, 12].

The combination of pure solvents as mixed solvents substantially increases the diversity of reaction media. The study of solvent effects on the chemical and physical processes in binary mixed solvent solutions is more complicated than in pure solvents, because the solute–solvent and solvent–solvent interactions can create new solvent properties leading to preferential solvation of the dissolved species. Preferential solvation occurs when the solutes interact more specifically with one of the components of the binary mixed solvent [13, 14].

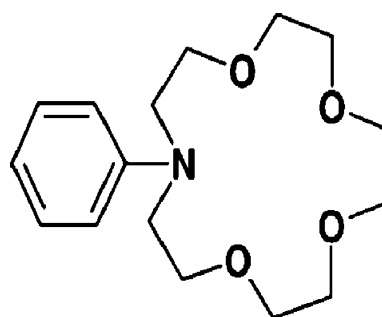
Studies of crown ethers complexation in different solvents show that the thermodynamic and kinetic parameters are affected by the nature and the composition of the solvent system [15–17]. Thermodynamic studies of macrocyclic complexation reactions with metal cations not only provide relevant information on the binding process, but also lead to a better understanding of the selective behavior of these ligands toward different metal cations.

It is of interest to us, therefore, to investigate the influence of the nature of the cation and ligand and also the composition of the solvent on the interactions between the metal cations with crown ethers in binary mixed non-aqueous solutions. In continuation of our previous works [18–21], here, we report the results of thermodynamic study for complexation reaction between PhA15C5 (Scheme 1) with UO_2^{2+} cation in acetonitrile–methanol (AN–MeOH), acetonitrile–butanol (AN–BuOH), acetonitrile–dimethylformamide (AN–DMF) and methanol–propylencarbonate (MeOH–PC) binary mixtures at different temperatures using conductometric method.

Experimental

Reagents and apparatus

N-phenylaza-15-crown-5 (PhA15C5) and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with the highest purity were purchased from Merck and were



Scheme 1 Structure of *N*-phenylaza-15-crown-5

used without any further purification except for vacuum drying. The purity of PhA15C5 was checked using NMR spectroscopy. The organic solvents (all from Merck) were used without further purification. Conductance measurements were performed using a digital Metrohm conductometer (model 712) in a water bath thermostated at a constant temperature which maintained within ± 0.1 °C. The electrolytic conductance was measured using a cell consisting of two platinum electrodes to which an alternating potential was applied. The calibration of conductometric cell was made with the use of an aqueous KCl solution and the cell constant was found to be of 0.75 cm^{-1} .

Procedure

The experimental procedure to obtain the stability constant of $(\text{PhA15C5} \cdot \text{UO}_2)^{2+}$ complex was as follows: a solution of metal salt ($1.0 \times 10^{-4} \text{ mol L}^{-1}$) 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 ($2.0 \times 10^{-3} \text{ mol L}^{-1}$) was carried out by a rapid transfer to the titration cell using a microburette and the conductance of the solution in the cell was measured after each transfer at the desired temperature.

Result and discussion

Conductance studies

In order to study the influence of adding PhA15C5 on the molar conductance of UO_2^{2+} cation in pure AN, MeOH, BuOH, DMF and PC and also in AN–MeOH, AN–BuOH, AN–DMF, and MeOH–PC binary mixtures, the conductivity of the solutions at a constant salt concentration ($1.0 \times 10^{-4} \text{ mol L}^{-1}$) was monitored while increasing the macrocycle concentration at various temperatures. The molar conductance versus ligand/cation mole ratio plots for $(\text{PhA15C5} \cdot \text{UO}_2)^{2+}$ complex in pure AN at different temperatures are shown in Fig. 1. As is seen from this Figure,

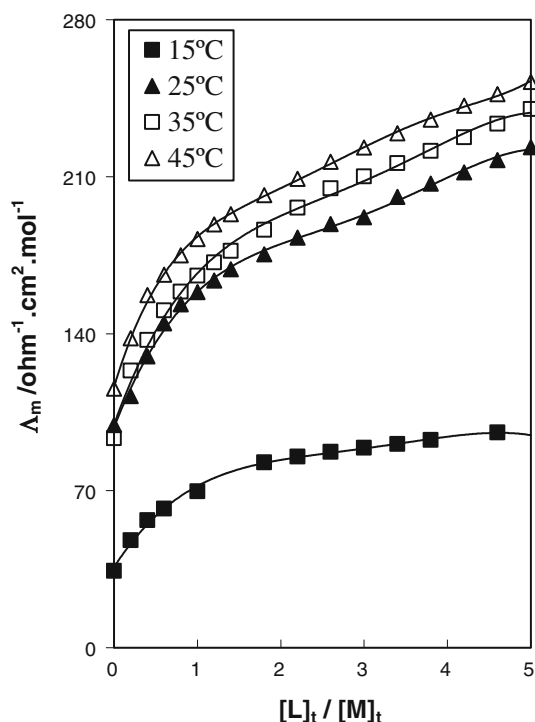


Fig. 1 Molar conductance–mole ratio plots for (PhA15C5·UO₂)²⁺ complex in pure AN at different temperatures

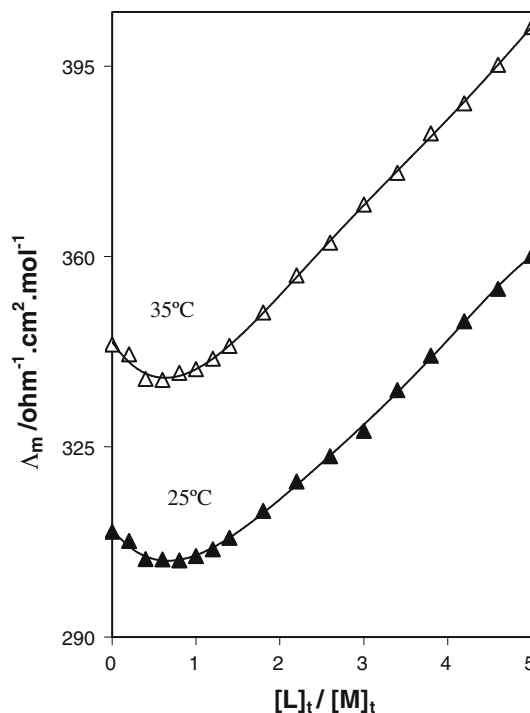
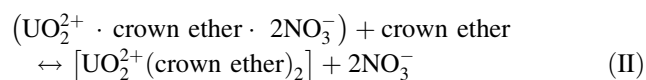
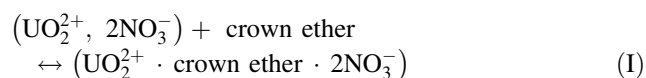


Fig. 2 Molar conductance–mole ratio plots for (PhA15C5·UO₂)²⁺ complex in pure MeOH at 25 and 35 °C

addition of PhA15C5 to UO₂²⁺ cation in pure AN at different temperatures shows an increase in molar conductivity, which indicates that the (PhA15C5·UO₂)²⁺ complex in this solvent is more mobile than free solvated UO₂²⁺ cation. Similar behavior was observed in most solvent systems.

In all cases, the slope of the corresponding molar conductivity versus [L]_t/[M]_t plots changes at the point where the ligand to cation mole ratio is about 1, which is an evidence for formation of a 1:1 complex between PhA15C5 and UO₂²⁺ cation in solution. Moreover, the entire resulting molar conductance–mole ratio data were fitted by [M:L] program, which further supports the formation of a 1:1 (ligand to metal ion) complex in solutions.

A very different behavior was observed for complexation of UO₂²⁺ cation with PhA15C5 in pure MeOH, PC and also in AN–MeOH (mol% MeOH = 75) and MeOH–PC (mol% MeOH = 75) binary solutions. As is obvious from Fig. 2, addition of PhA15C5 to UO₂²⁺ cation in pure MeOH causes the molar conductivity to decrease until the mole ratio reaches 1:1 and then to increase. Such behavior may be described according to the following equilibria:



It seems that addition of PhA15C5 to UO₂²⁺ cation solution results in formation a 1:1 [M:L] complex which is present as ion-pair (I). Further addition of the ligand to the ion-pair complex, results in formation of a 1:2 [M:L₂] complex with a sandwich structure which decreases the space for diffusion and interaction of NO₃⁻ with UO₂²⁺ cation which results in dissociation of the ion-pair (II) and, therefore, the molar conductivity increases.

These results reveal that the stoichiometry of the complex formed between PhA15C5 and UO₂²⁺ cation changes with the nature and also the composition of the solvent system. Similar results have been obtained for complexation of uranyl cation with diaza-15-crown-5 and aza-18-crown-6 in AN–MeOH binary solvent systems [20–22].

The stability constant of (PhA15C5·UO₂)²⁺ complex at each temperature was obtained from variation of molar conductance as a function of [L]_t/[M]_t molar ratios using a GENPLOT computer program [23]. The details of calculation of the stability constants of complexes by the conductometric method have been described elsewhere [21–25]. The values of the stability constant (logK_f) for (PhA15C5·UO₂)²⁺ complex in various solvent systems are listed in Table 1. It should be noted that, in the process of calculation of formation constant of complex, due to the highly dilute experimental conditions used in this study, it was assumed that the association of UO₂²⁺ cation and NO₃⁻ anion into ion pair is negligible.

Table 1 Log K_f values of $(\text{PhA15C5}\cdot\text{UO}_2)^{2+}$ complex in AN–MeOH, AN–BuOH, AN–DMF and MeOH–PC binary mixtures at different temperatures

Medium	Log $k_f \pm \text{SD}^a$			
	15 °C	25 °C	35 °C	45 °C
AN–MeOH				
Pure AN	4.47 ± 0.10	3.91 ± 0.10	3.92 ± 0.10	3.90 ± 0.10
75% AN–25% MeOH ^b	2.81 ± 0.10	3.87 ± 0.06	3.56 ± 0.07	3.78 ± 0.08
50% AN–50% MeOH	3.15 ± 0.08	3.71 ± 0.05	3.57 ± 0.09	3.38 ± 0.09
25% AN–75% MeOH	c	c	c	c
Pure MeOH	c	c	c	c
AN–BuOH				
Pure AN	4.47 ± 0.10	3.91 ± 0.10	3.92 ± 0.10	3.90 ± 0.10
75% AN–25% BuOH ^b	3.77 ± 0.05	3.78 ± 0.06	3.57 ± 0.04	3.82 ± 0.06
50% AN–50% BuOH	4.01 ± 0.03	3.89 ± 0.04	3.78 ± 0.05	3.62 ± 0.06
25% AN–75% BuOH	3.30 ± 0.07	3.13 ± 0.05	3.42 ± 0.02	3.34 ± 0.04
Pure BuOH	2.75 ± 0.10	2.82 ± 0.08	2.86 ± 0.10	2.75 ± 0.08
AN–DMF				
Pure AN	4.47 ± 0.10	3.91 ± 0.10	3.92 ± 0.10	3.90 ± 0.10
75% AN–25% DMF ^b	3.29 ± 0.04	2.94 ± 0.06	2.76 ± 0.09	2.81 ± 0.10
50% AN–50% DMF	3.29 ± 0.05	2.89 ± 0.05	2.78 ± 0.10	2.70 ± 0.10
25% AN–75% DMF	2.81 ± 0.08	c	2.77 ± 0.09	2.62 ± 0.04
Pure DMF	2.73 ± 0.10	2.63 ± 0.06	2.78 ± 0.09	c
MeOH–PC				
Pure MeOH	c	c	c	c
75% MeOH–25% PC ^b	c	c	c	c
50% MeOH–50% PC	c	2.75 ± 0.30	2.82 ± 0.10	3.17 ± 0.06
25% MeOH–75% PC	3.17 ± 0.20	c	3.59 ± 0.03	3.84 ± 0.06
Pure PC	3.35 ± 0.20	c	3.59 ± 0.03	3.84 ± 0.06

^a *SD* standard deviation

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

^c The data can not be fitted to equations

Effect of temperature

As is evident in Table 1, the stability constant of $(\text{PhA15C5}\cdot\text{UO}_2)^{2+}$ complex decreases with increasing the temperature in most of the solvent systems, which is an evidence for an exothermic complexation reaction between PhA15C5 with UO_2^{2+} cation in solutions, but in the case of MeOH–PC binary mixtures, the stability constant of this complex increases with increasing the temperature, therefore, the complexation process between PhA15C5 with UO_2^{2+} cation is endothermic in these binary solutions.

Effect of solvent composition

As is evident in Table 1, the stability constant of $(\text{PhA15C5}\cdot\text{UO}_2)^{2+}$ complex in pure non-aqueous solvents decreases in the order: AN>PC>BuOH>DMF which is consistent with the inverse order of their solvating abilities

as expressed by the Gutmann donor number. Since the donor ability of acetonitrile molecules (DN = 14.1) is lower than PC (DN = 15.1), BuOH (DN = 19.0) and DMF (DN = 26.6), therefore, the complex is more stable in AN solution compared with the other pure organic solvents. It has been shown that the solvating ability of a solvent, as expressed by the Gutmann donocity scale [26], plays a fundamental role in complexation reactions [27].

Comparison of the data in Table 1, reveals that, the stability of $(\text{PhA15C5}\cdot\text{UO}_2)^{2+}$ complex in the binary mixed solvent solutions varies in the order: AN–BuOH>AN–MeOH>AN–DMF which can be attributed to the inherent solvating ability of the pure solvents which form the binary mixtures. DMF with a relatively high donor ability (DN = 26.6) relative to MeOH (DN = 20.0) and BuOH (DN = 19.0) can solvate the UO_2^{2+} cation strongly and compete with the ligand for this cation in solution. In addition, the higher dielectric constant of DMF ($\epsilon = 36.7$)

compared with MeOH ($\epsilon = 32.6$) and BuOH ($\epsilon = 18.0$) could also lead to a decrease in electrostatic interactions between PhA15C5 and UO_2^{2+} cation in solution.

As is seen from Figs. 3 and 4, the change of the stability constant ($\log K_f$) of $(\text{PhA15C5}\cdot\text{UO}_2)^{2+}$ complex with the composition of AN–MeOH and AN–DMF binary systems is not linear. A non-linear behavior was also observed for other binary solutions. This behavior may be due to the interactions between the methanol and acetonitrile molecules via hydrogen bonding and the strong dipolar interactions between acetonitrile and dimethylformamide molecules in their binary mixtures, which results in changing the structure and properties of the mixed solvents and, therefore, changing the solvation of the cation, the ligand and the resulting complex in these binary solvent solutions.

The interactions between some binary mixed solvents have been studied [28]. For example, mixing of dimethylformamide with acetonitrile, induces the mutual destruction of dipolar structures of these dipolar aprotic solvents and releasing the free dipoles [29]. As a result, strong dipolar interaction between acetonitrile and dimethylformamide molecules is expected.

The preferential solvation of UO_2^{2+} cation, the ligand, the resulting complex and even the counter ion and the characteristics of its changes with the composition of the

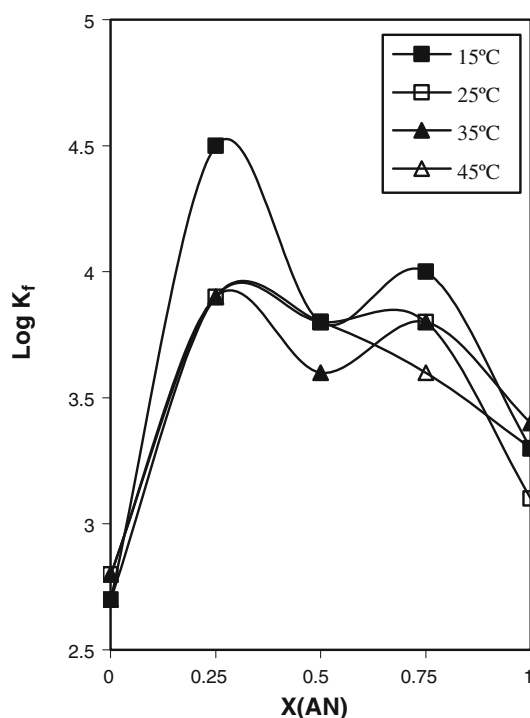


Fig. 3 Changes of the stability constant ($\log K_f$) of $(\text{PhA15C5}\cdot\text{UO}_2)^{2+}$ complex with the composition of AN–MeOH binary system at different temperatures

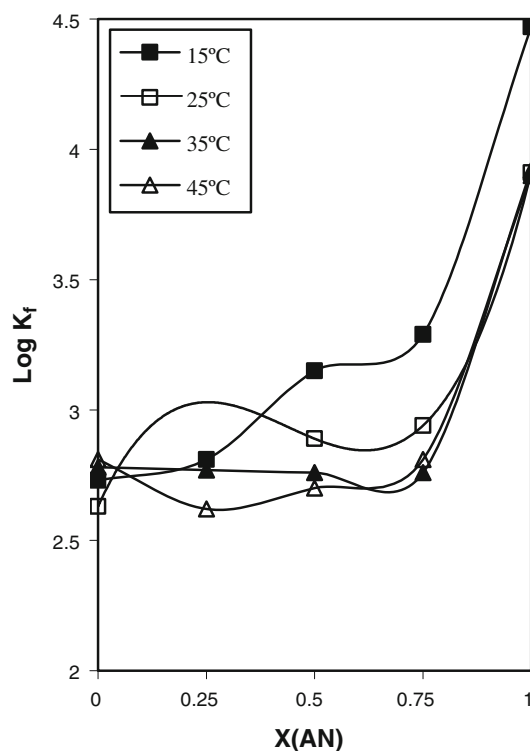


Fig. 4 Changes of the stability constant ($\log K_f$) of $(\text{PhA15C5}\cdot\text{UO}_2)^{2+}$ complex with the composition of AN–DMF binary system at different temperatures

mixed solvents may be another reason for this kind of behavior. In mixed solvents, the energetic effect of the preferential solvation depends quantitatively on the structural and energetic properties of the mixtures [30]. In addition, the non-monotonic behavior observed for changes of $\log K_f$ of $(\text{PhA15C5}\cdot\text{UO}_2)^{2+}$ complex with the composition of the mixed solvents, probably reflects a balance between the solvation properties, donicity, hydrogen bonding ability, etc of the solvent systems.

Thermodynamic calculations

In order to have a better understanding of thermodynamics of complexation reactions of the metal cations with the ligands, it is useful to determine the contribution of enthalpy and entropy of the reactions. The ΔH_c° and ΔS_c° values for complexation process between PhA15C5 and UO_2^{2+} cation were determined from the temperature dependence of the stability constant of $(\text{PhA15C5}\cdot\text{UO}_2)^{2+}$ complex using the van't Hoff plots. In all cases, the plots of $\ln K_f$ versus $1/T$ were linear. The values of standard enthalpies for complexation reaction 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 values of the standard entropies were calculated from

Table 2 Thermodynamic parameters for (PhA15C5·UO₂)²⁺ complex in AN–MeOH, AN–BuOH, AN–DMF and MeOH–PC binary mixtures

Medium	$\Delta G^\circ \pm SD^a$ (kJ mol ⁻¹)	$\Delta H^\circ \pm SD^a$ (kJ mol ⁻¹)	$\Delta S^\circ \pm SD^a$ (J mol ⁻¹ K ⁻¹)
AN–MeOH			
Pure AN	-22.31 ± 0.30	-34.87 ± 11.03	c
75% AN–25% MeOH ^b	-22.11 ± 0.10	57.50 ± 6.80	253.82 ± 6.80
50% AN–50% MeOH	-21.19 ± 0.20	-30.54 ± 2.10	-31.1 ± 0.03
AN–BuOH			
Pure AN	-16.09 ± 0.09	c	84.38 ± 2.80
75% AN–25% BuOH ^b	-21.61 ± 0.60	c	81.99 ± 0.90
50% AN–50% BuOH	-22.23 ± 0.10	-22.15 ± 1.40	c
25% AN–75% BuOH	-17.87 ± 0.80	c	73.97 ± 20.61
Pure BuOH	-16.09 ± 0.09	c	84.38 ± 2.80
AN–DMF			
Pure AN	-22.31 ± 0.30	-34.87 ± 11.03	c
75% AN–25% DMF ^b	-16.81 ± 0.20	-47.16 ± 5.81	-100.9 ± 19.53
50% AN–50% DMF	-16.51 ± 0.10	-33.87 ± 4.50	-57.52 ± 15.27
25% AN–75% DMF	-16.02 ± 5.40	c	c
Pure DMF	-15.02 ± 0.30	c	66.97 ± 1.20
MeOH–PC			
50% MeOH–50% PC ^b	-15.69 ± 0.90	38.64 ± 13.10	180.32 ± 42.6

^a *SD* standard deviation

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

^c With high uncertainty

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 thermodynamic data given in Table 2, reveal that depending on the solvent composition, the sign of the enthalpy values for formation of (PhA15C5·UO₂)²⁺ complex is negative or positive. These results show that the complexation process between PhA15C5 and UO₂²⁺ cation is exothermic (favorable) or endothermic (unfavorable) depending on the nature and composition of the mixed solvents. In most cases, positive values of ΔS°_c characterize the formation of this complex. Hence, the (PhA15C5·UO₂)²⁺ complex is stabilized from entropy viewpoint. The two main factors, which affect the ΔS°_c values, are (i) the loss of conformational entropy of ligand upon complexation and (ii) the randomness of the solvent molecules in bulk solvent after being released during desolvation of metal cation and the ligand. It has been reasonably assumed that the negative entropy changes upon complexation are related to a change in the conformational entropy of the ligand from a rather flexible structure in the free state to a rigid conformation in the complex [31]. The release of some solvent molecules after desolvation process of the cation and the ligand also contributes to the positive entropy values [32].

As is obvious from Table 2, the standard thermodynamic quantities (ΔH°_c , ΔS°_c) are quite sensitive to the nature and composition of the mixed solvents and a

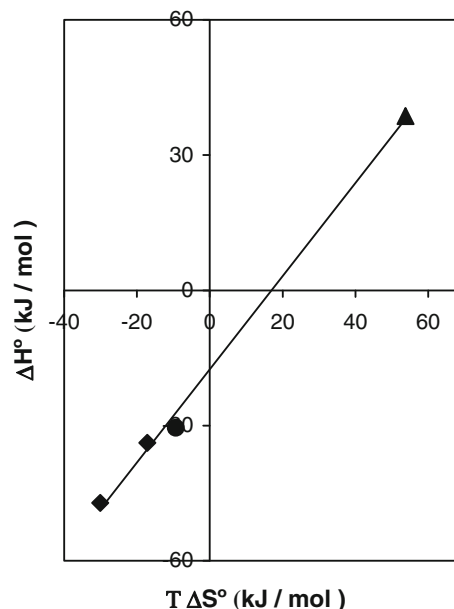


Fig. 5 Plot of the ΔH° versus $T\Delta S^\circ$ for (PhA15C5·UO₂)²⁺ complex in different binary mixed solvents: (filled diamond AN–DMF, filled circle AN–MeOH, filled triangle MeOH–PC)

non-monotonic behavior is observed between these thermodynamic functions and the composition of the binary solutions. This behavior is due to the variations in the extent of the contribution of such important parameters as

solvation-desolvation of the species involved in the complexation reaction (i.e., cation, macrocycle and the resulting complex), and also the conformational changes of the macrocyclic ligand with the composition of solutions. Therefore, we should not expect a monotonic relationship between these thermodynamic quantities and the solvent composition. Similar behaviors have already been reported for various metal cation-crown ether complexes in different binary mixed solvents [18–22, 30].

In most cases, the observed increase (or decrease) in ΔH° value upon addition of a pure solvent to the solvent mixture will be compensated by an increase (or decrease) in the corresponding ΔS° value. The existence of such a compensating effect (Fig. 5) between ΔH° and ΔS° values, which has been frequently reported for a variety of metal–ligand systems [33, 34], would cause the overall change in the ΔG° value of the complex to be smaller than might be expected from the change in either ΔH° or ΔS° independently.

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