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Conductometric Determination of Formation Constants of tris(2-pyridyl)methylamine and Titanium (III) in Water-Acetonitryl Mixture

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A conductance study of the interaction between titanium (III) cation and tris(2-pyridyl) methylamine (tpm), in water-acetonitrile mixtures was carried out at various temperatures. The formation constants of the resulting 1:1 complexes were determined from the molar conductance-mole ratio data. The stability constants of 1:1 (M:L) complexes of tpm with titanium (III) cation, the Gibbs standard free energies (ΔG_c^o), the standard enthalpy changes (ΔH_c^o) and the standard entropy changes (ΔS_c^o) for the formation of these complexes in acetonitrile–water (AN–H_2O) binary mixtures have been determined conductometrically. The stability constants of the complexes were obtained from fitting of molar conductivity curves using a computer program, GENPLOT.

Keywords: Tris(2-pyridyl) methylamine; Titanium (III); Acetonitrile–water; Conductometry.

1. INTRODUCTION

Tripodal ligands based on nitrogen heterocycles are one of the most widely used groups of macrocyclic compounds and play a key role in inorganic chemistry. The first preparation of poly-pyrazolylborate coordination compounds emerged during the 1960s with Trofimenko [1]. In the past two decades, however, other types of tripodal nitrogen ligands had been given an increasing attention. Following this, the coordination chemistry of tris(2-pyridyl) ligands has recently been reviewed [2]. In

2000, Arnold et al. published a paper in which they described the synthesis of tpm and set out the coordination chemistry of tpm and related species and their amine derivatives with copper and zinc [3].

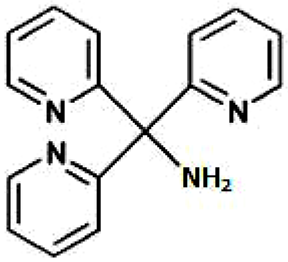
Titanium is present in aqueous solution, such as $Ti(OH)_6^{3+}$, $Ti(OH)(OH_2)_5^{2+}$, $Ti_2O(OH_2)_{10}^{4+}$, $Ti(OH)_{3+x}$ (x corresponding to the oxidation rate) and TiO_2 [4]. The dissolution and hydrolysis of titanium chloride (III), used as a source of titanium, are multivariate processes. The existence of each of these species is dependent on different variables, such as pH, temperature, titanium concentration and hydrochloric acid concentration [5]. In this research, the $Ti(OH)(OH_2)_5^{2+}$ cation prevailed in acidic solution (pH = 1-3) while another species was dominant in different pH values of titanium aqueous solution [5-7].

$$\begin{array}{lcccc} & Ti(OH)_6^{3+} \leftrightarrow & Ti(OH)(OH_2)_5^{2+} \leftrightarrow & Ti_2O(OH_2)_{10}^{4+} \leftrightarrow & Ti(OH)_{3+x} \\ \text{pH} & < 1 & 1\text{-}3 & 3 & 3 < \end{array}$$

All the measured solutions had a pH range of 1 to 3. It was expected that the dominant titanium species in the crystal structure of titanium chloride (III) to be in the form of $Ti(OH)(OH_2)_5^{2+}$. This finding was further supported and approved by the literature [3].

Many physico-chemical techniques have been used to study the complexation reactions between macrocyclic compounds with different metal cations in solutions such as potentiometry [8], calorimetry [9], conductometry [10], NMR spectroscopy [11], spectrophotometry [12] and polarography [11].

For obtaining the appropriate solvent properties, mixtures of two solvents were often used. In these mixed solvent systems, many chemical and electrochemical reactions might be carried out advantageously due to the fact that the physiochemical properties of mixed solvents are interesting both from theoretical and practical points of view. Usually, mixed solvents do not behave as expected from statistical considerations; hence, the solvating ability of solvents in mixtures can be different from those of neat media [13]. The extent of preferential solvation and the existence of specific solvent–solute and solvent–solvent interactions are due to the deviations from ideal behaviour [14].



Scheme 1. tris(2-pyridyl) methylamine (tpm)

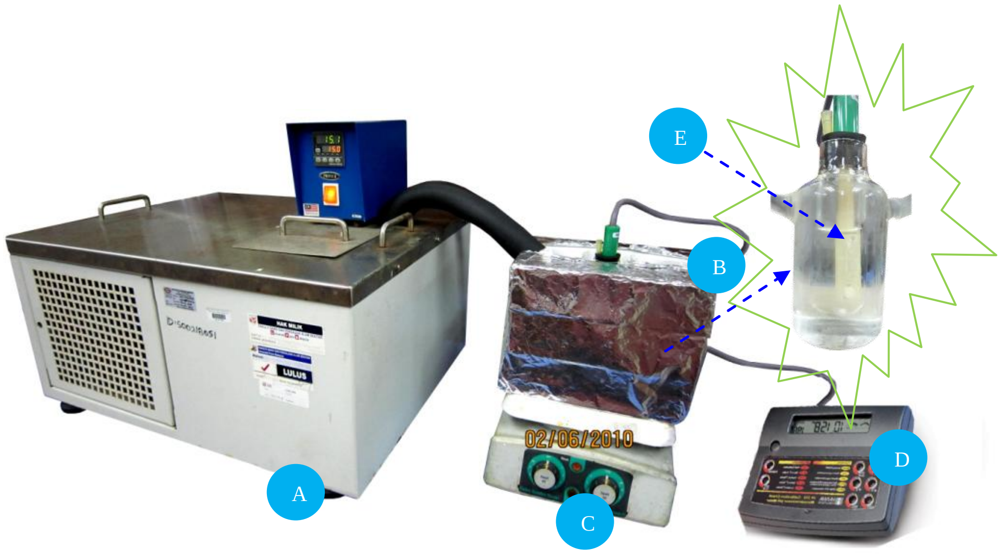
In this paper, the results of the thermodynamic study and the selectivity for complexation reactions between tris(2-pyridyl) methylamine (tpm) (scheme 1) with $Ti(OH)(OH_2)_5^{2+}$ cation in acetonitrile–water (AN–H_2O) binary mixtures at different temperatures using the conductometric method and also the effect of macrocyclic ligand (tpm) by the nature of titanium cation, substituent in the ligand and by the composition of acetonitrile–water binary solution as a purpose, were investigated.

To the best of our knowledge, this is the first reported research on thermodynamic study of titanium (III) ion using the conductometric method. The findings from this paper can be used for many applications of titanium (III), such as fabrication of ion selective electrode based on macrocyclic ionophores for determining titanium (III) cation in real samples.

2. EXPERIMENTAL

A $TiCl_3$ solution of about 15% (Merck) was used without further purification. Deionized bi-distilled water was used throughout this experiment. Acetonitrile from Merck was also used with the highest purity. In addition, tpm as an ionophore was synthesized and purified according to the literature [3].

In this work, n-Butyllithium was added drop wise to a solution of 2-aminomethylpyridine in dry THF at -70°C in N_2 gas. The temperature of the mixture was allowed to rise slowly to room temperature and was then stirred for 24 h. 2-Chloropyridine was added drop wise to the resulting violet mixture and stirred for 8 h. Water was added and the mixture was stirred for 30 min. The volatile components were removed in vacuo and CH_2Cl_2, and then water was added to the residue. The layers were separated and the aqueous layer was extracted with CH_2Cl_2. The organic layers were dried over $MgSO_4$ and reduced in vacuo. The resulting oil was triturated with Et_2O–hexane (1:1) to solidify it, which was recrystallised in water.



Scheme 2. Conductometeric instruments. A) water bath, B) water-jacketed cell, C) magnetic mixer, D) conductometer, E) conductivity electrode

The experimental procedure to obtain the formation constant of the complex was as follows. A solution of titanium chloride (III) (5.0×10^{-5} M) was placed in a titration cell and the conductance of the solution was measured. Then the tpm concentration was increased by adding the tpm solution in the same solvent (2.5×10^{-3} M) to the titration cell using a microburette, and the conductance of the resulted solution was measured after each step at the desired temperature. The conductance measurements were performed on a digital Hanna conductivity apparatus (Model HI 255) in a thermostated water-bath with a constant temperature maintained within ±0.01°C. The electrolytic conductance was measured using a cell made of the platinum black to which an alternating potential was applied. A conductometric cell with a cell constant of 0.99 cm^{-1} was used throughout the studies. The schematics of the water-jacketed cell and the measuring instruments include: cell, water-bath thermostated, conduct electrode and conductometer are illustrated in scheme 2.

3. RESULT AND DISCUSSION

Changes in molar conductivity (Λ_m) versus the ligand-to-cation molar ratio ($[L]_t/[M]_t$) for the complexation of tpm with the $Ti(OH)(OH_2)_5^{2+}$ cation were measured in pure AN and water and in AN–H_2O binary systems at different temperatures. In the study, $[L]_t$ is the total concentration of the ligand, while $[M]_t$ is the total concentration of the titanium cation.

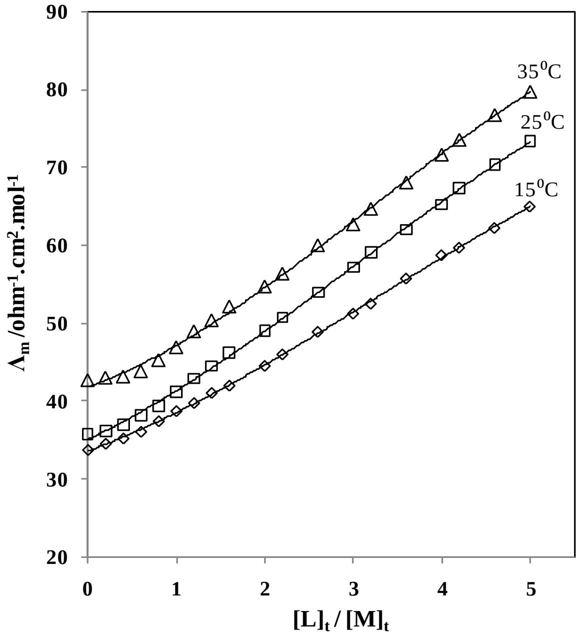


Figure 1. Molar conductance–mole ratio plots for the (tpm-$Ti(OH)(OH_2)_5)^{2+}$ complex in pure AN at different temperatures.

Four typical series of molar conductance values as a function of ligand/metal cation mole ratios in pure AN, H_2O and AN–H_2O (mole% AN = 18.68, 57.95) binary mixtures are shown in figures 1, 2, 3 and 4, respectively. In addition, the stability constant of tpm complex in different solvent mixtures at various temperatures was obtained from variation of molar conductance as a function of ligand/metal cation mole ratios using a GENPLOT computer program [15].

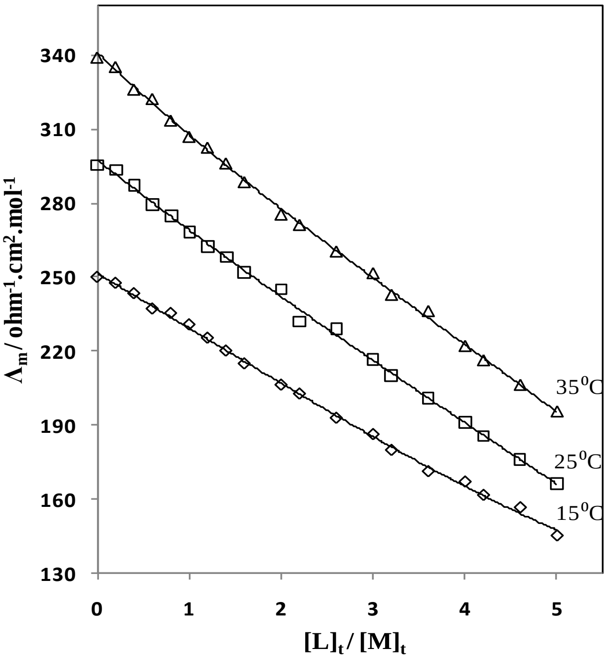


Figure 2. Molar conductance–mole ratio plots for the (tpm-Ti(OH)(OH_2)$_5$)$^{2+}$ complex in pure H_2O at different temperatures.

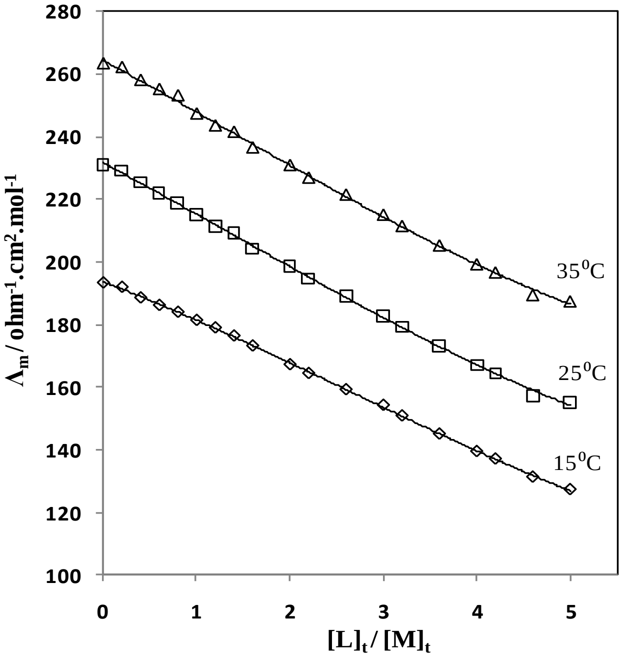


Figure 3. Molar conductance–mole ratio plots for the (tpm-Ti(OH)(OH_2)$_5$)$^{2+}$ complex in AN–H_2O binary mixture (mol% AN=18.68) at different temperatures.

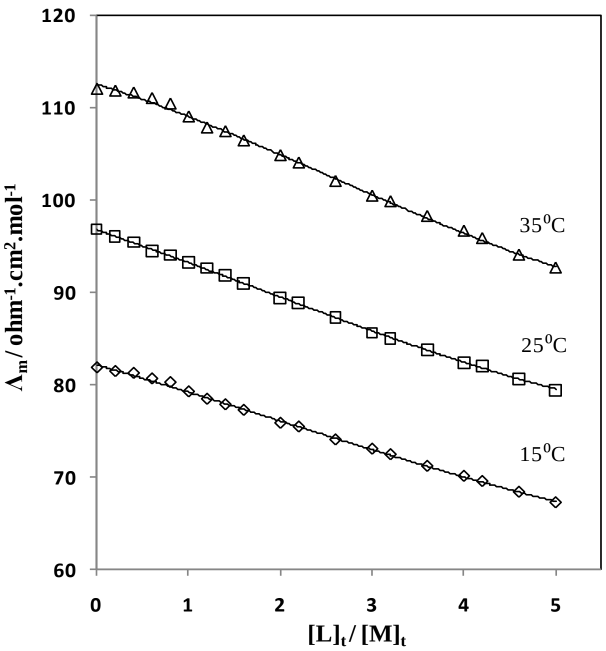


Figure 4. Molar conductance-mole ratio plots for the (tpm-Ti(OH)$(OH_2)_5$)$^{2+}$ complex in AN–H_2O binary mixture (mol% AN=57.95) at different temperatures.

The details of calculation of the stability constants of complexes by the conductometric (mole% AN = 57.95, 18.68) binary mixture at different temperatures showed a gradual decrease in molar conductivity with an increase in the ligand concentration.

Table 1. Log K_f values of tpm. Ti(OH)$(OH_2)_5^{2+}$ complex in AN–H_2O binary mixtures at different temperatures

Medium	Log K_f ± SD[a]		
	15^{0}C	25^{0}C	35^{0}C
Pure AN	2.45±0.027	2.27±0.050	1.87±0.075
57.95% AN-42.05% H_2O[b]	2.60±0.021	2.88±0.078	2.47±0.020
34.09% AN-65.91% H_2O	2.67±0.023	2.70±0.088	2.85±0.120
18.68% AN-81.32% H_2O	2.68±0.089	2.74±0.120	2.79±0.130
7.93% AN-92.07% H_2O	2.84±0.130	2.85±0.130	2.88±0.100
Pure H_2O	2.43±0.150	2.77±0.170	2.78±0.110

[a] SD = Standard deviation

[b] The composition of each solvent system is expressed in mole% of each solvent

This behaviour indicated that the tpm complex was less mobile than the free solvated Ti(OH)$(OH_2)_5^{2+}$ cation. Similar behaviour was observed in all other solvent systems. However, as seen in figure 1, the addition of tpm to Ti(OH)$(OH_2)_5^{2+}$ cation in pure AN system at different temperatures resulted in an increase in molar conductivity, which indicated that the tpm-Ti(OH)$(OH_2)_5^{2+}$ complex in this solution was more mobile than the free solvated Ti(OH)$(OH_2)_5^{2+}$ cation. The slope of the corresponding molar conductivity versus the ligand/cation mole ratio plots changed at the point where the ligand to cation mole ratio was about one, which was evidence for the formation of a 1:1 [M:L] complex in the solution.

As evident in table 1, the stability constant of tpm-Ti(OH)$(OH_2)_5^{2+}$ complex increased with the increase in the temperature in most of the solvent systems, which was evidence for an endothermic complexation reaction between tpm with Ti(OH)$(OH_2)_5^{2+}$ cation in the solutions. However, in the case of pure AN solvent, the stability constant of this complex decreased with the increase in temperature; therefore, the complexation process between tpm with Ti(OH)$(OH_2)_5^{2+}$ cation was exothermic in these binary solutions.

As apparent in table 1, the stability constant of (tpm-Ti(OH)$(OH_2)_5)^{2+}$ complex in various pure solvents at 25^0C decreased in order: H_2O > AN. In spite of the medium donor ability of acetonitrile (DN = 14.1), the stability of the (tpm-Ti(OH)$(OH_2)_5)^{2+}$complex in pure AN was lower than the pure H_2O and AN-H_2O binary solutions. Notably, tris(2-pyridyl) methylamine (tpm) is a fairly rigid, electron rich, bowl-like host; therefore, it is suitable for the complexation of cationic, aromatic and organic guests via stacking and charge transfer interactions, as well as via hydrogen bonding.

It has been reported that the acetonitrile molecules interact strongly with the tpm molecules. Thus, the behaviour observed in these two solvent systems was probably due to the interactions between the tpm and AN molecules, which involved the hydrogen bonding between CH_3 protons, while AN involved nitrogens in tpm [16]. These interactions of tpm-acetonitrile were stronger than that of tpm-water. This conclusion was further confirmed by higher solubility of tpm in acetonitrile, while it only dissolved in boiling water.

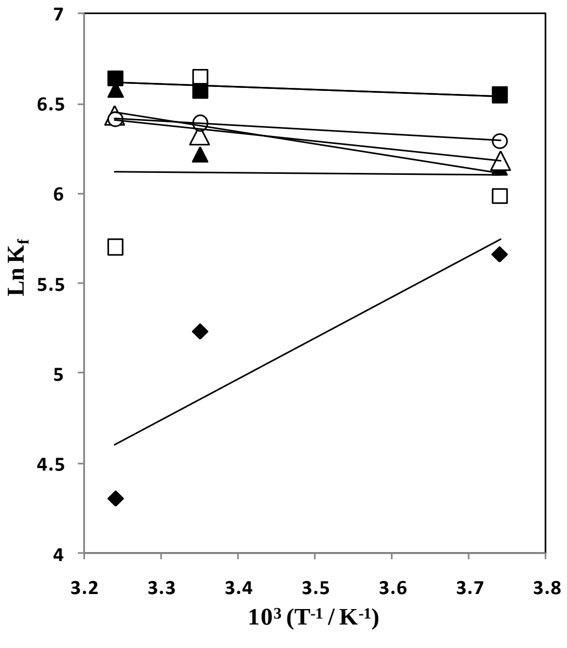


Figure 5. Van't Hoff plots for (tpm-Ti(OH)$(OH_2)_5)^{2+}$ complex in AN–H_20 binary systems: (mol% AN: ♦ 100, □ 57.95, ▲ 34.09, Δ 18.68, ■ 7.93,○ 0.00).

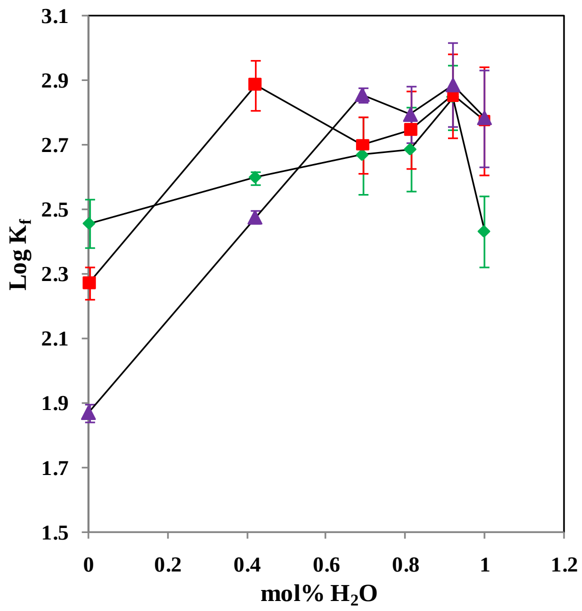


Figure 6. Changes of the stability constant (log K$_f$) of (tpm-Ti(OH)(OH$_2$)$_5$)$^{2+}$ complex with the composition of AN–H$_2$O binary systems at different temperatures: (♦15^0 C, ■ 25^0 C, ▲ 35^0 C).

Moreover, another reason was that, since titanium (III) ion is a soft acid [17], it interacted with the nitrogen atom of the acetonitrile molecule as a soft base; therefore, the titanium (III) ion was solvated to a higher extent in the AN solvent [18].

As seen in figure 6, the changes of the stability constant (log K$_f$) of (tpm-Ti(OH)(OH$_2$)$_5$)$^{2+}$ complex versus the composition of AN–H$_2$O binary system at various temperatures were not linear. This behaviour was probably due to some kind of solvent–solvent interactions between these two solvents; hence, it changed the structure of the solvent mixtures and subsequently altered the solvation properties of the titanium (III) cation, the tpm and even the resulting complex in solutions. In addition, the heteroselective solvation of these species in these mixed solvents might be another reason for this kind of behaviour. Notably, the interactions between some binary mixed solvents have been studied. For example, the mixing of dimethylformamide with acetonitrile induced the mutual destruction of dipolar structures of these dipolar aprotic liquids, releasing the free dipoles [18]. As a result, a strong dipolar interaction between acetonitrile and water molecules was expected.

The van’t Hoff plots of lnK$_f$ versus 1/T for all of the investigated systems were constructed. A typical example of these plots is shown in figure 5. The changes in the standard enthalpy (ΔH_c^o) for the complexation reactions were obtained from the slope of the van’t Hoff plots, and the changes in the standard entropy (ΔS_c^o) were calculated from the following relationship [20].

$$\Delta G^0_{c,298.15} = \Delta H^0_{c,298.15} - 298.15\Delta S^0_c$$

The experimental values of standard enthalpy (ΔH_c^o) and standard entropy (ΔS_c^o), which are given in table 2, showed that in most cases, the (tpm-Ti(OH)(OH$_2$)$_5$)$^{2+}$ complex was enthalpy destabilized but entropy stabilized. Therefore, the entropy of the complexation reaction is the principal driving force for the formation of this complex in most solvent systems. However, in the case of pure AN solvent, the values of standard enthalpy for the complexation process were negative. Therefore, the (tpm-Ti(OH)$(OH_2)_5)^{2+}$ complex was stabilized from the enthalpy viewpoint in the pure AN solvent.

Table 2. Thermodynamic parameters for (tpm-Ti(OH)$(OH_2)_5)^{2+}$ complex in AN–H_2O binary mixtures

Medium	$-\Delta G_c^o \pm$ SD[a] kJ/mol	$\Delta H_c^o \pm$ SD[a] kJ/mol	$\Delta S_c^o \pm$ SD[a] J/mol °K
Pure AN	12.97±2.90	-85.30±8.30	-242.60±26.10
57.95% AN-42.05% H_2O[b]	16.48±0.44	34.06±8.73	169.55±29.24
34.09% AN-65.91% H_2O	15.41±0.50	2.96±1.27	61.66±3.90
18.68% AN-81.32% H_2O	15.68±0.67	9.03±0.43	82.90±1.72
7.93% AN-92.07% H_2O	16.29±0.74	3.16±1.41	65.25±4.03
Pure H_2O	15.84±0.97	4.35±1.50	67.73±3.85

[a] SD = Standard deviation

[b] The composition of each solvent system is expressed in mole% of each solvent

The experiment results showed that in majority of cases, the change in standard enthalpy for the complexation reaction between Ti(OH)$(OH_2)_5^{2+}$ cation and tpm was negligible; therefore, it seemed that the complexation processes in most of the solvent systems were probably athermic. But in the case of pure AN solvent, the complexation reaction was exothermic.

4. CONCLUSIONS

The stability constant for the complexation of titanium ion with tris(2-pyridyl) methylamine in 0.00, 7.93, 18.68, 34.09, 57.95 and 100 acetonitrile-water (mole%) binary solvents were determined conductometrically at different temperatures. According to the obtained results, the compression of the formation constant (at identical temperature) showed that in most of the cases, the stability constant of the complex increased with the increasing water percentage. Determination of thermodynamic parameters showed the negative value of ΔG_c^o to prove the ability of the ligand to form stable complexes and the process trend to proceed spontaneously. However, the obtained negative value of ΔH_c^o in pure acetonitrile means that enthalpy was the driving force for the formation of the complex, but in other systems, this express was opposite. Furthermore, the positive values of ΔS_c^o indicated that entropy was responsible for the complexing process in most of the cases, whereas in the case of pure acetonitrile, enthalpy played this role.

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